Large scale ab initio calculations for carrier dynamics and electron transports in organic and organic/inorganic mixed systems

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INCITE Project
NERSC, NCCS, ALCF

Outline

(1) Hole hopping transport in random P3HT polymer

(2) Electron transport between connected quantum dots

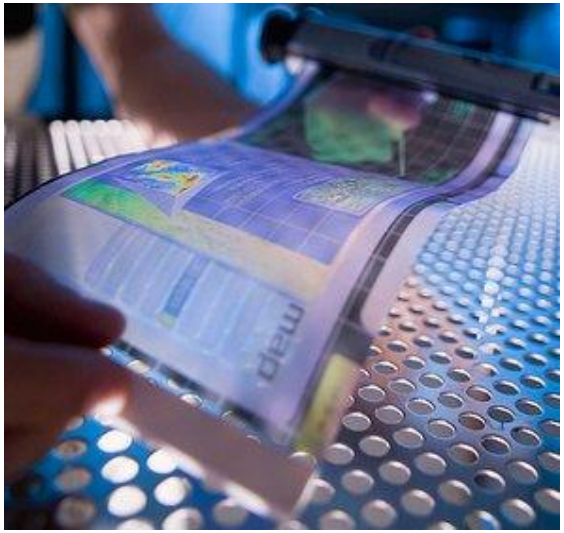
(3) Time-domain simulations

Acknowledgment

Nenad Vukmirovic (P3HT polymer)
Iek Heng Chu, Marina Radulaski (QD-QD transport)
Jifeng Ren (time domain simulation)

Why study hole transport in random polymers ?

- Conducting polymers (e.g., P3HT) have been used for solar cells, and OLED
- But the theoretical study of the conductivity has been in the phenomenological level
- Want to change it to ab initio level



What we need to do?

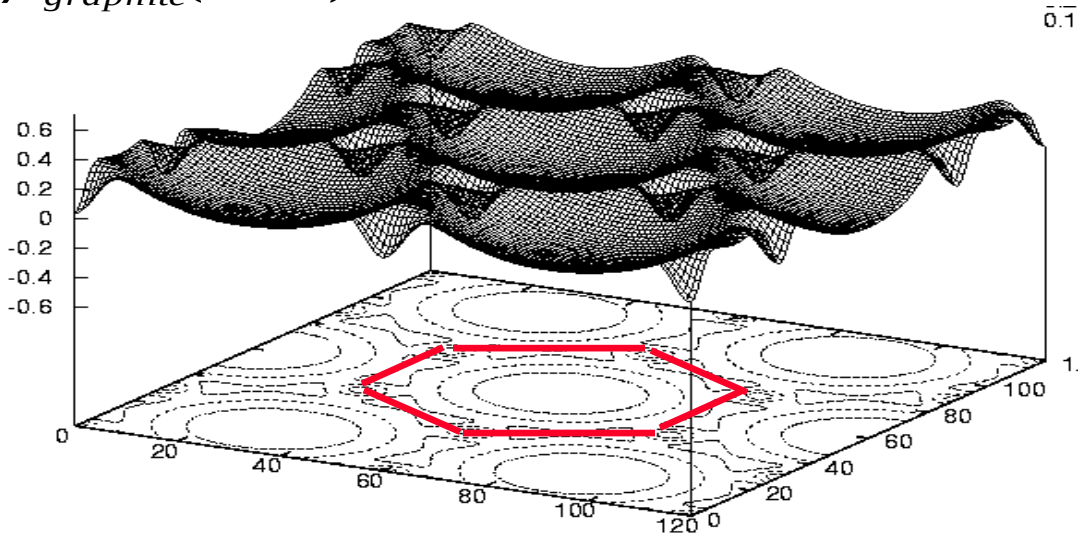
(1) 1000 to 10,000 atom systems

(2) electron-phonon interactions

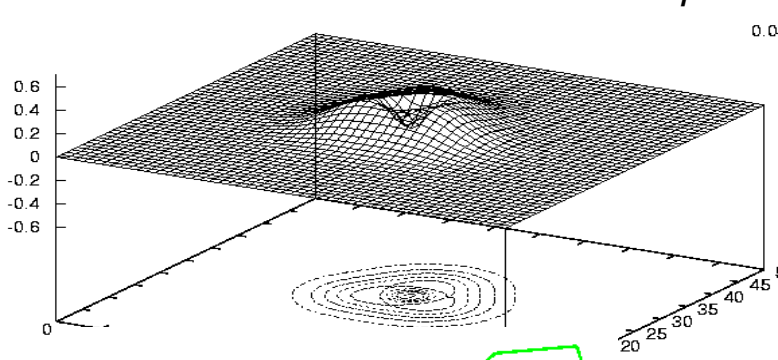
Motif based charge patching method

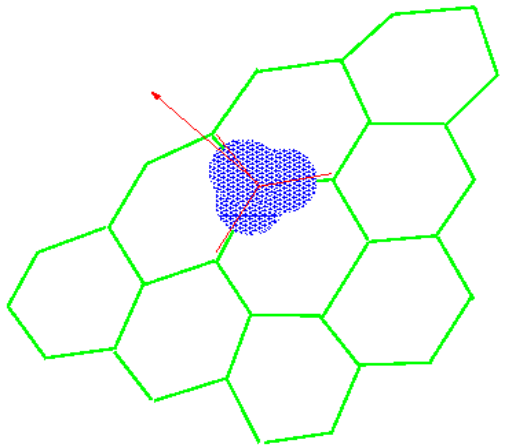
$$\rho_{motif}(r) = \rho_{graphite}(r) \times \frac{\rho_{atom}(r - R_0)}{\sum_R \rho_{atom}(r - R)}$$

$\rho_{graphite}(LDA)$



ρ_{motif}





$$\rho^{patch}_{nanotube}(r) = \sum_R \rho^{aligned}_{motif}(r - R)$$

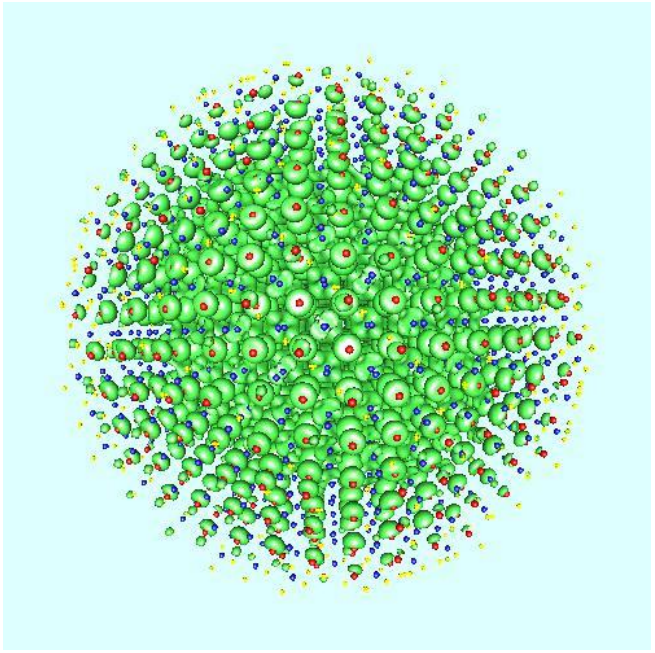
Error: 1%, ~20 meV eigen energy error.

Charge patching: free standing quantum dots

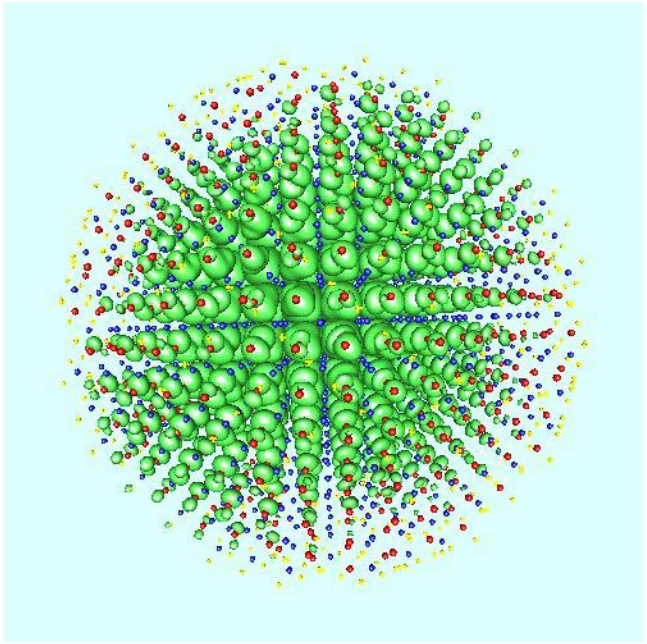
$In_{675}P_{652}$ LDA quality calculations (eigen energy error ~ 20 meV)

64 processors (IBM SP3) for ~ 1 hour

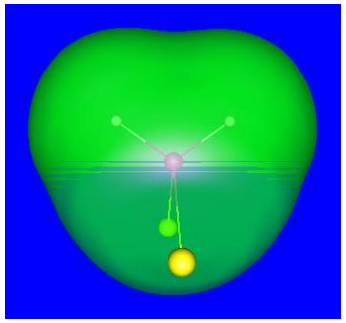
CBM

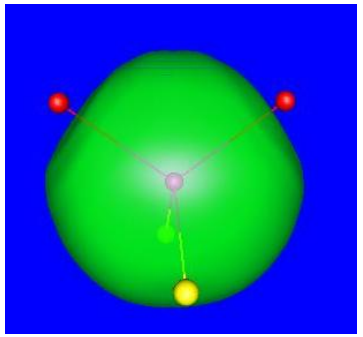


VBM



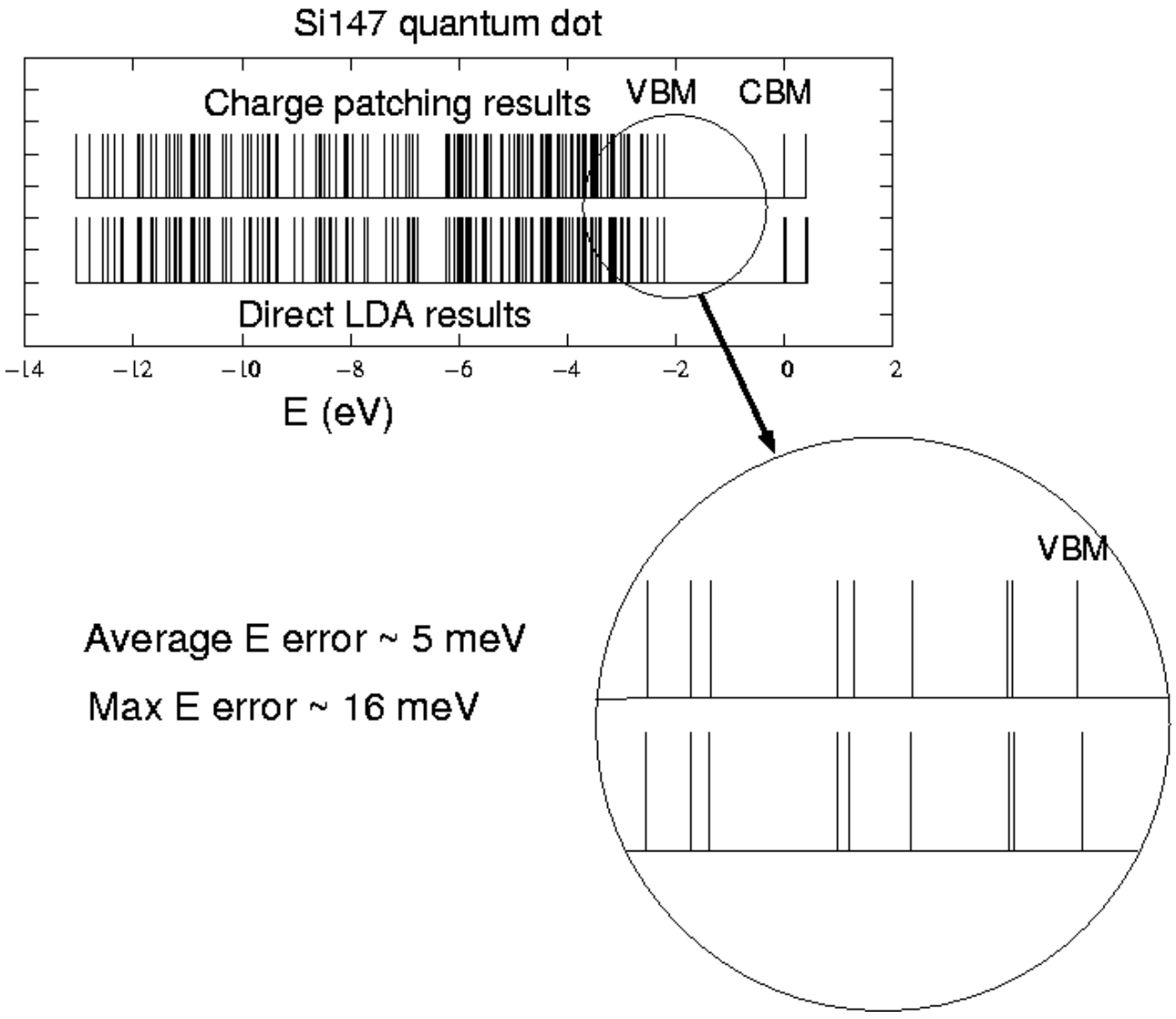
Total charge density motifs





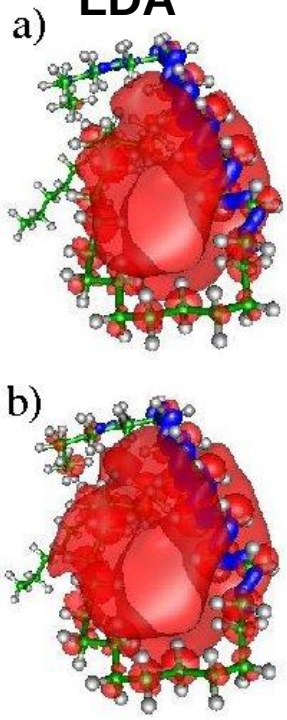
The band edge eigenstates are calculated using linear scaling folded spectrum method (FSM), which allows for 10,000 atom calculations.

The accuracy for the small Si quantum dot

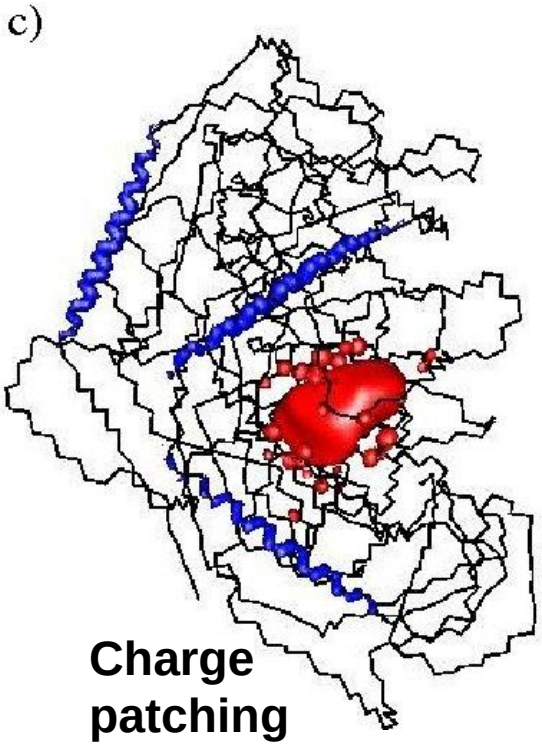


Charge patching for organic molecules

Direct LDA



Charge patching



Charge patching

Tested:
alkanes, alkenes, acenes
thiophenes,furanes,pyrroles,
PPV

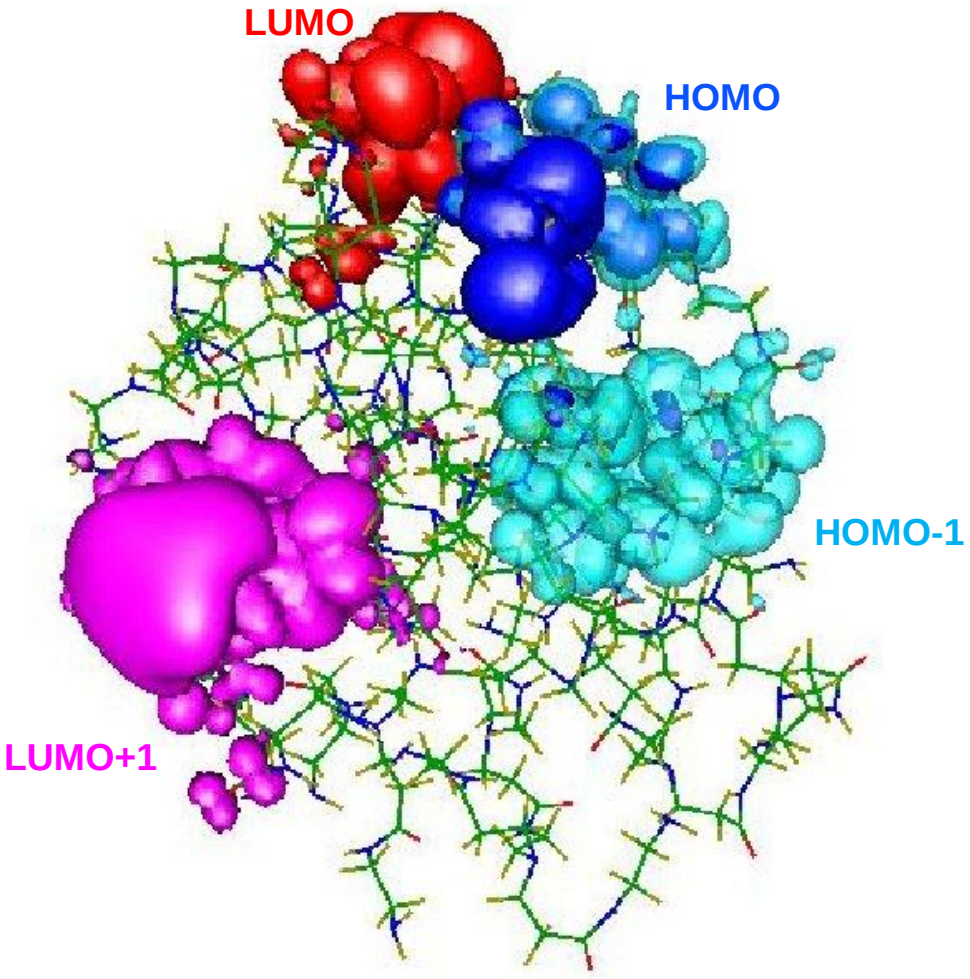
Different length and configurations

Typical eigen energy error is less than 30 meV

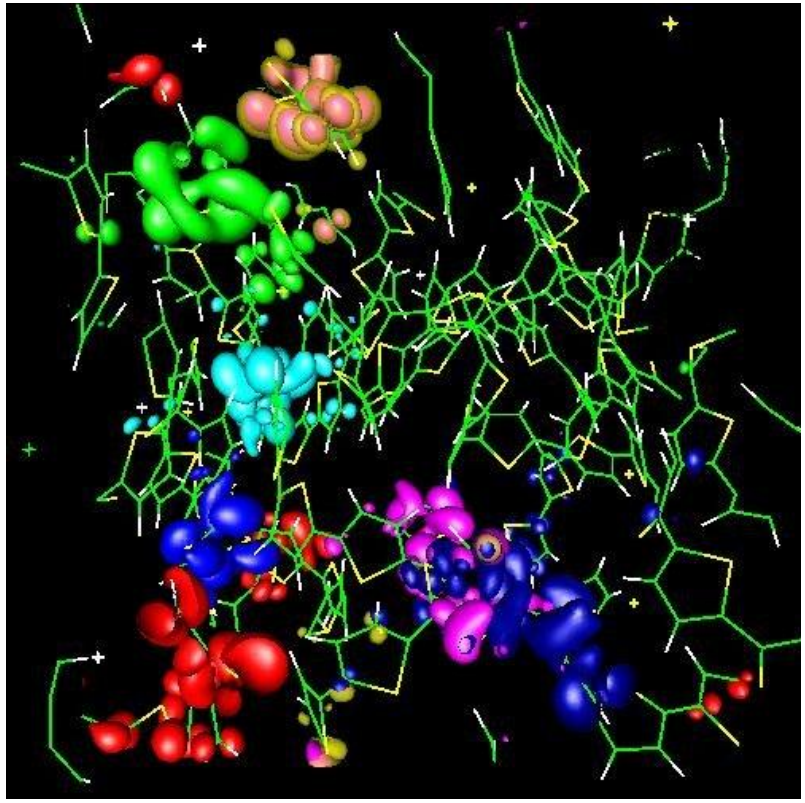
Red: LUMO (CBM); Blue: HOMO(VBM)

Long Alkane chain.

Electron states in other organic systems (charge patching)



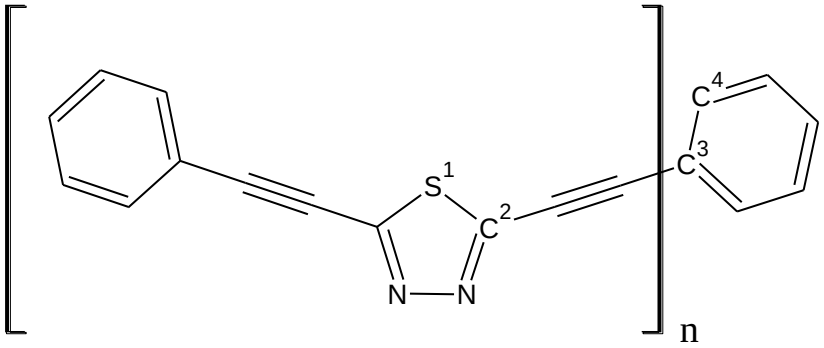
A 3 generation PAMAM dendrimer



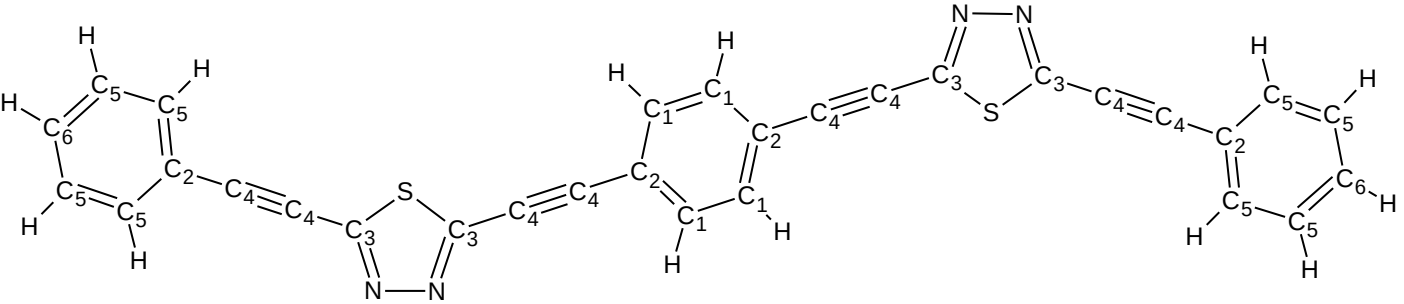
An amorphous P3HT blend

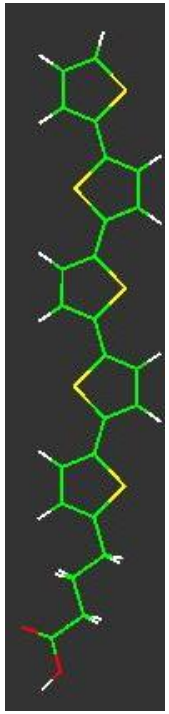
A few examples of organic systems

a)

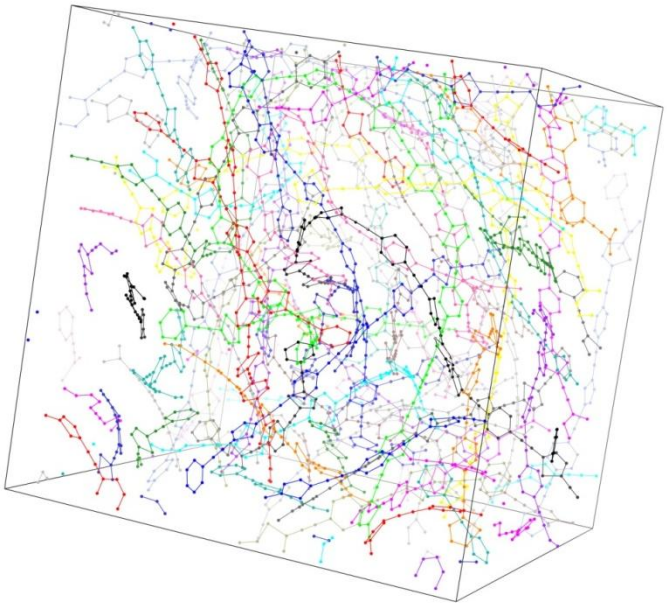


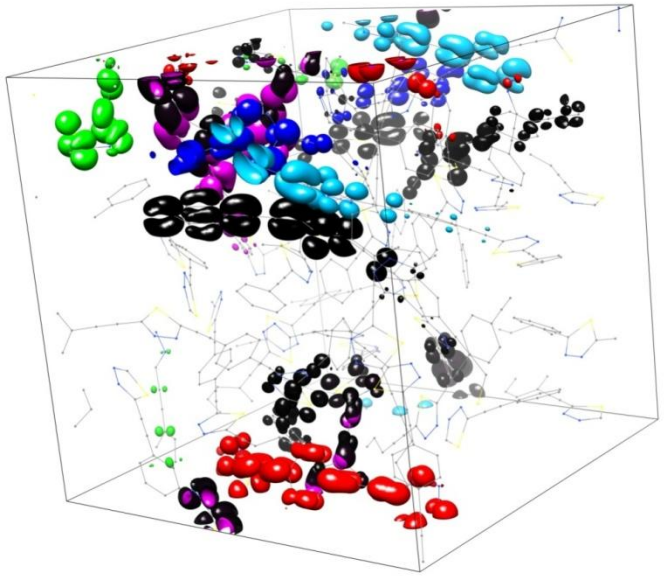
b)



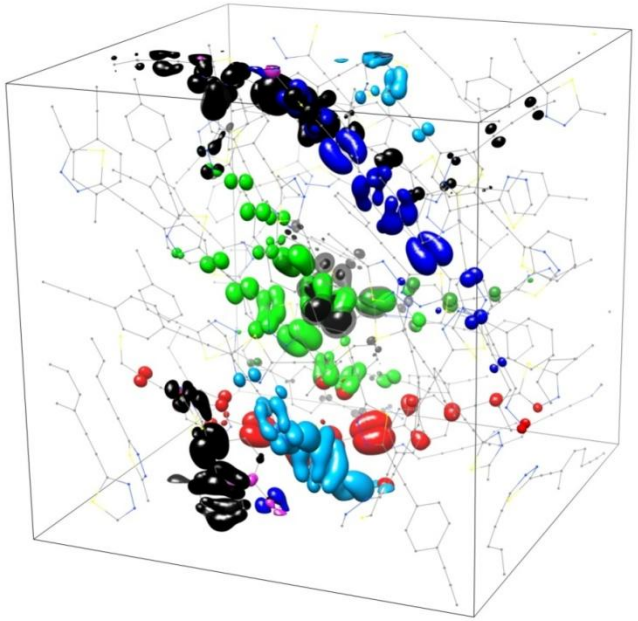


PhEtTh electronic states





CB states



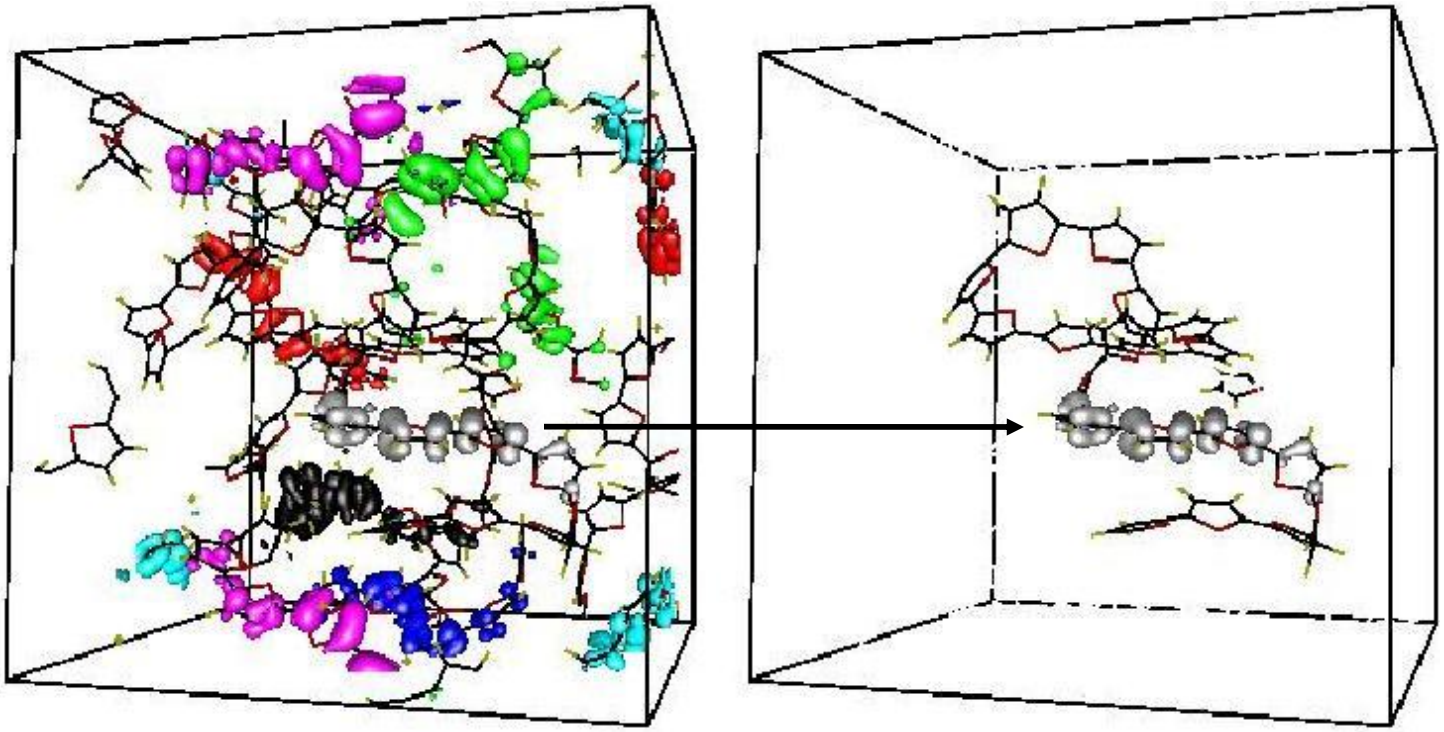
VB states

Hole Wave functions in P3HT

- typically localized to 3-6 rings.
- weakly affected by other chains.

P3HT – 5 chains with 20 rings (2510 atoms)

blue: 18.910eV
green: 18.888eV
cyan: 18.755eV
red: 18.690eV
pink: 18.682eV
black: 18.675eV
white: 18.654eV



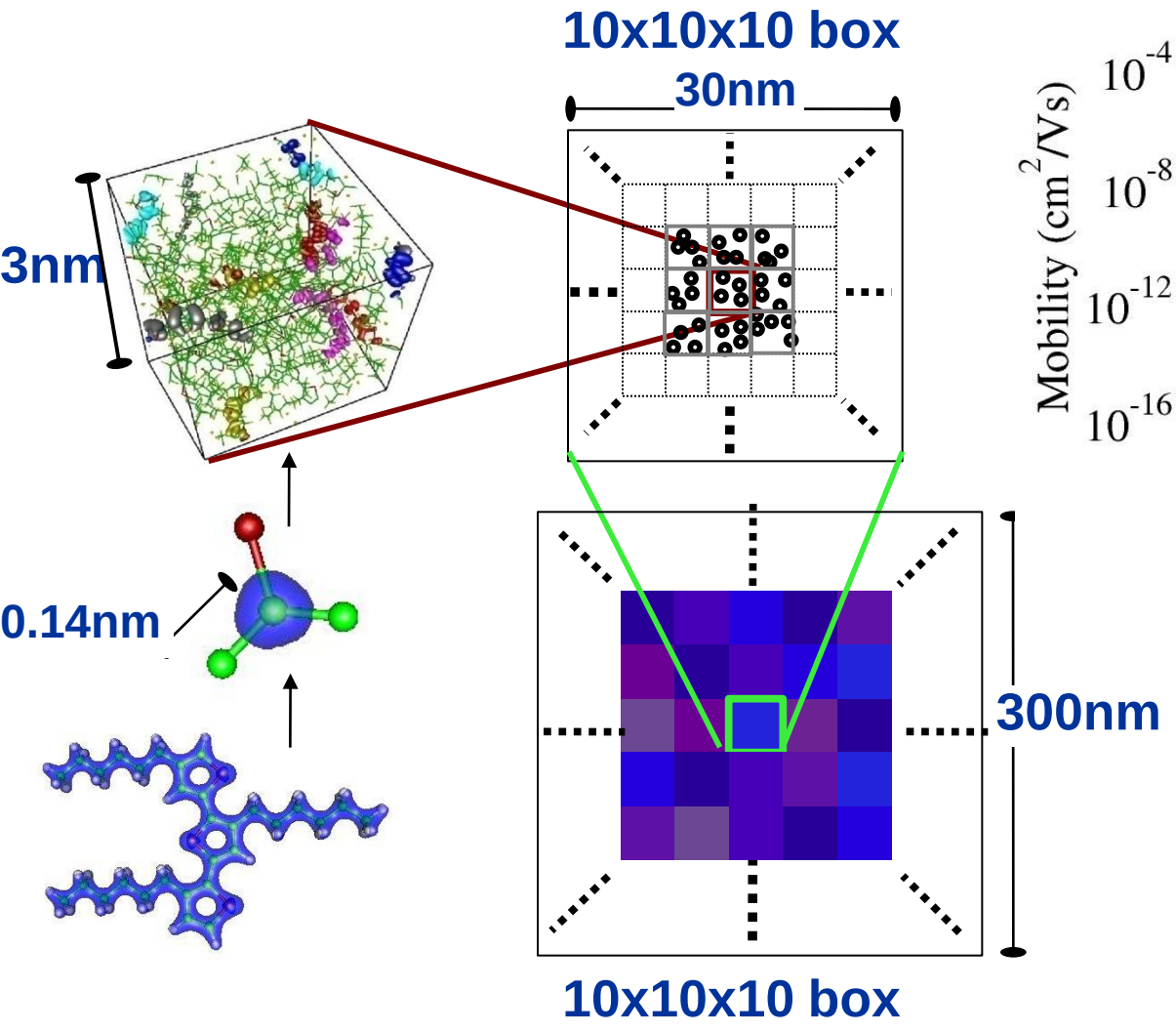
Explicit calculation of localized states and their transition rates

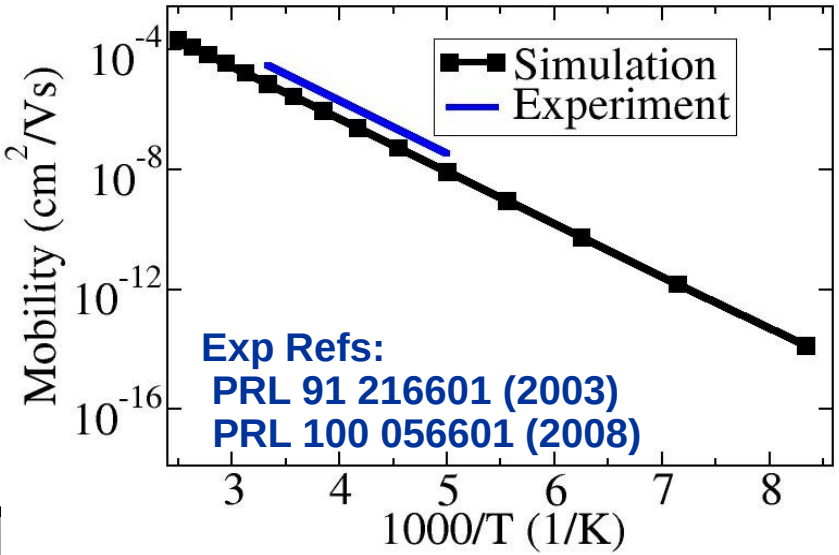
- Classical force field MD for P3HT blend atomic structure
- Take a snapshot of the atomic structure
- CPM and FSM to calculate the electronic states ψ_i.
- Classical force field calculation for all the phonon modes
- Quick CPM calculation for electron-phonon coupling constants $C_{i,j}(\upsilon) = \langle \psi_i \,|\, \partial H / \partial \upsilon \,|\, \psi_j \rangle$
- transition rate W_{ij} from $C_{ij}(v)$:

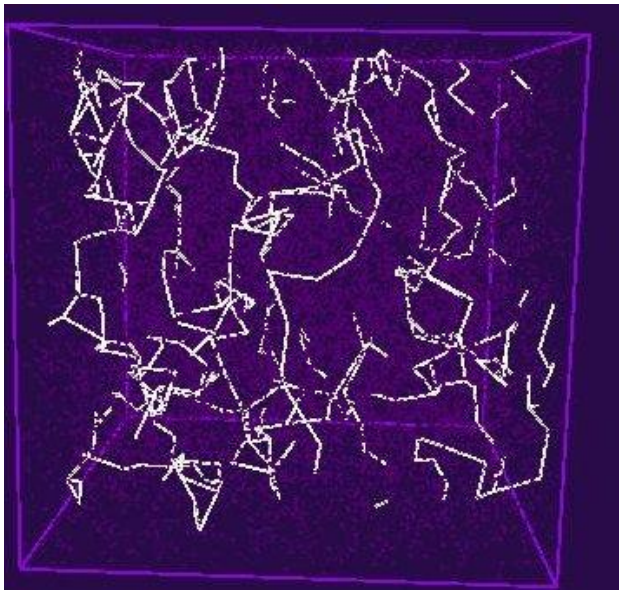
$$W_{ij} = \sum_{\nu} |\, C_{ij}(\nu) \,|^2 \, [n_\nu + 1/2] \delta(\varepsilon_i - \varepsilon_j - \hbar\omega_\nu) + ..$$

- using W_{ij} and multiscale approach to simulate carrier transport

Multiscale model for electron transport in random polymer







How good is the phenomenological model ?

The Miller-Abrahams model for weak electron-electron hopping rate

$$W_{ij} = C \exp(-\alpha R_{ij}) \begin{cases} \exp(-(\varepsilon_j - \varepsilon_i)/kT) & \text{for } \varepsilon_j > \varepsilon_i \\ 1 & \text{for } \varepsilon_j < \varepsilon_i \end{cases}$$

Full calculations and three different models

Full Calc.

$$W_{ij}^{F} = \sum_{\alpha} M_{ij,\alpha}^{2}[N(\varepsilon_{ij})+1]\frac{1}{\varepsilon_{ij}}\delta(\varepsilon_{ij}-\omega_{\alpha})$$

$$M_{ij,\alpha} = \langle \psi_i | \partial H / \partial \nu_{\alpha} | \psi_j \rangle$$

Model A

$$W_{ij}^{A} = \beta^{2} S_{ij}^{2}[N(\varepsilon_{ij})+1]\frac{1}{\varepsilon_{ij}} D_{ph}(\varepsilon_{ij})$$

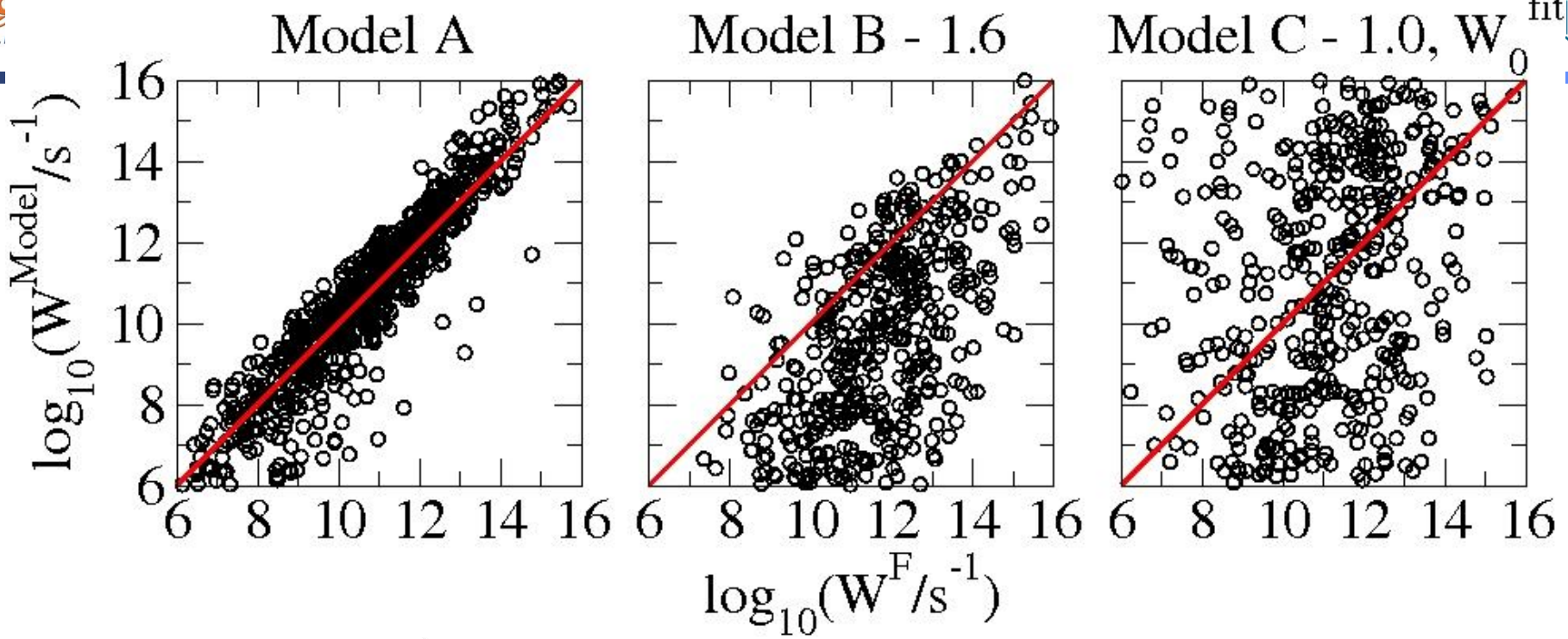
$$S_{ij} = \int |\psi_i \| \psi_j| d^{3}r$$

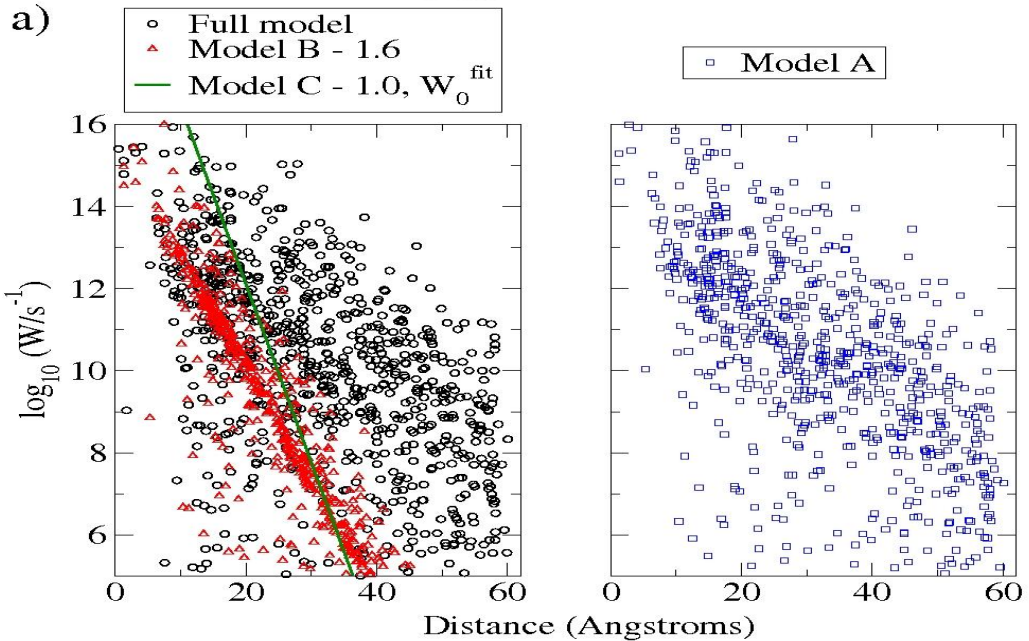
Model B

$$W_{ij}^{B} = \beta^{2} \exp(-d_{ij}/a)[N(\varepsilon_{ij})+1]\frac{1}{\varepsilon_{ij}} D_{ph}(\varepsilon_{ij})$$

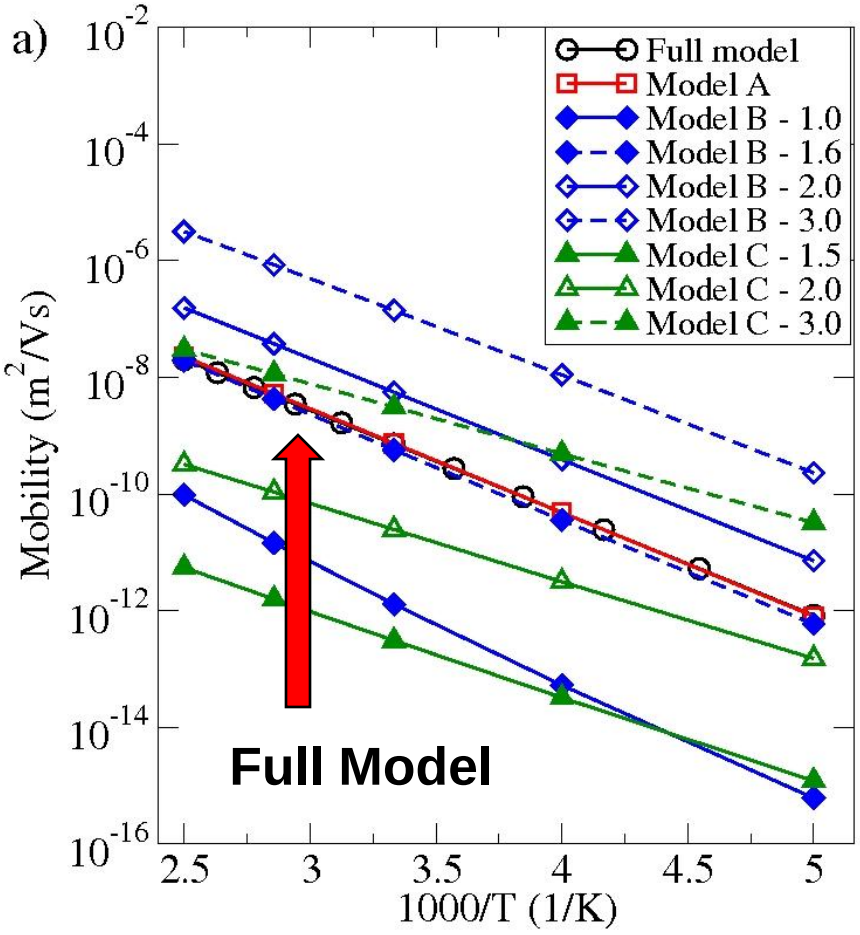
Miller model (Model C)

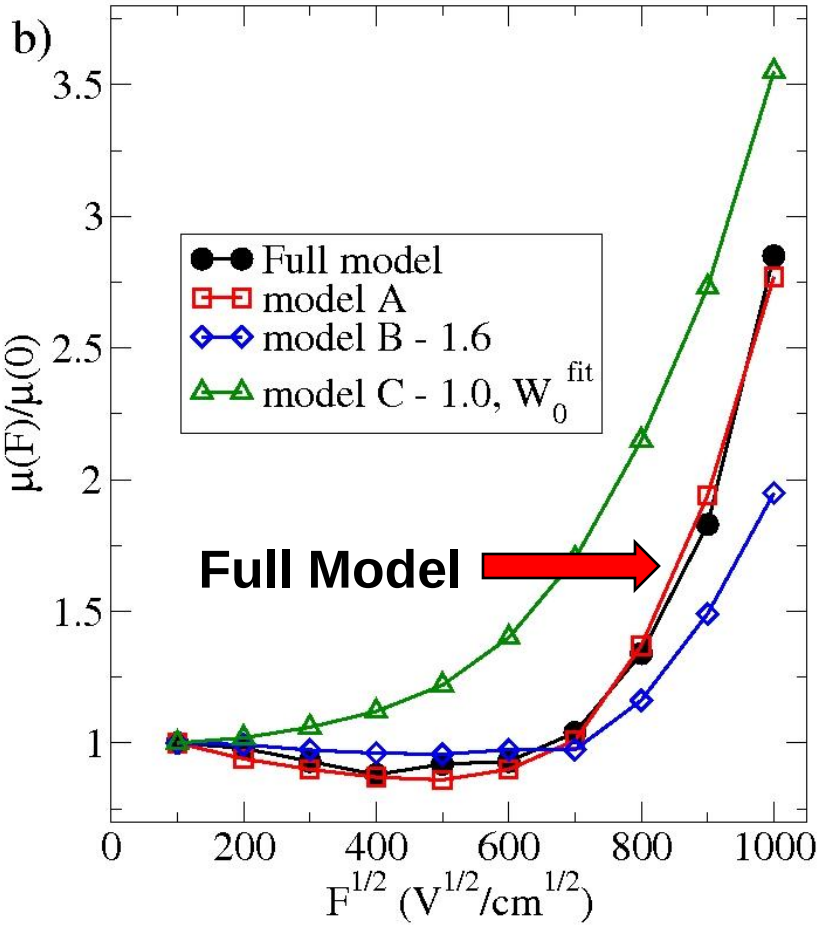
$$W_{ij}^{C} = W_0 \exp(-d_{ij}/a)$$


Model A
Model B - 1.6
Model C - 1.0, W0fit
log10(WModel/s-1)
log10(WF/s-1)
6
8
10
12
14
16


a)
Full model
Model B - 1.6
Model C - 1.0, W0fit
Model A
log10 (W/s-1)
Distance (Angstroms)
0
20
40
60
6
8
10
12
14
16

Field dependent mobility

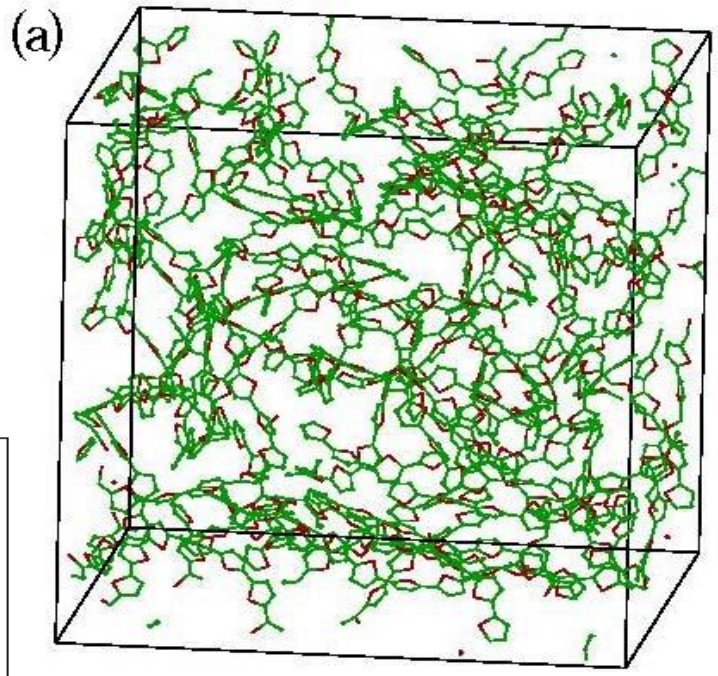


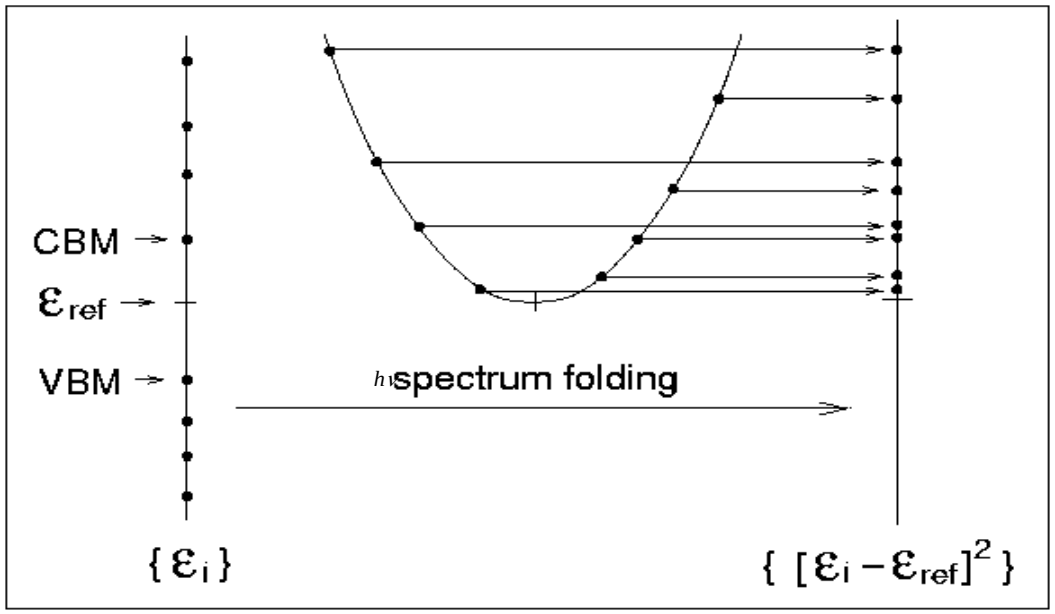


F: electric field (E)

Calculating the electronic states for a given H

- The system contains 10,000 atoms, more than a million PW basis set.
- Calculate the electronic structures using folded spectrum method (it is doable, but time consuming.



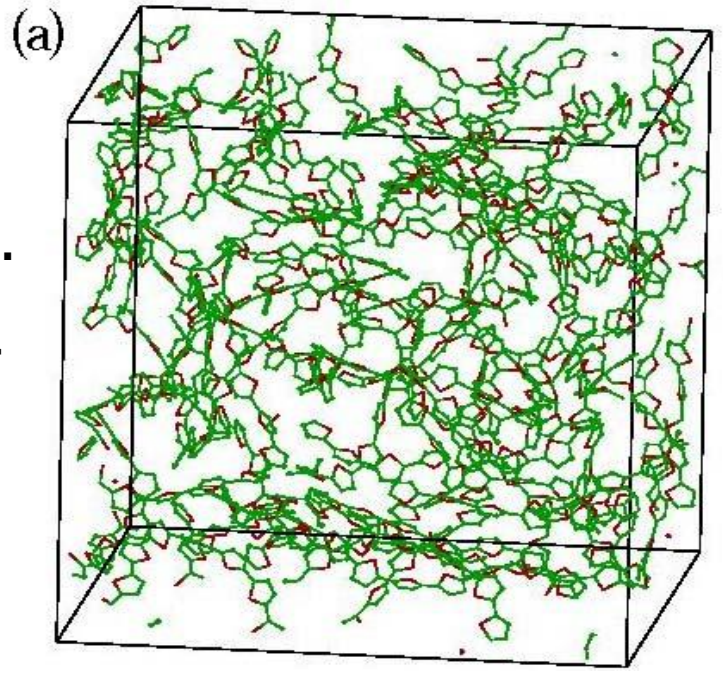


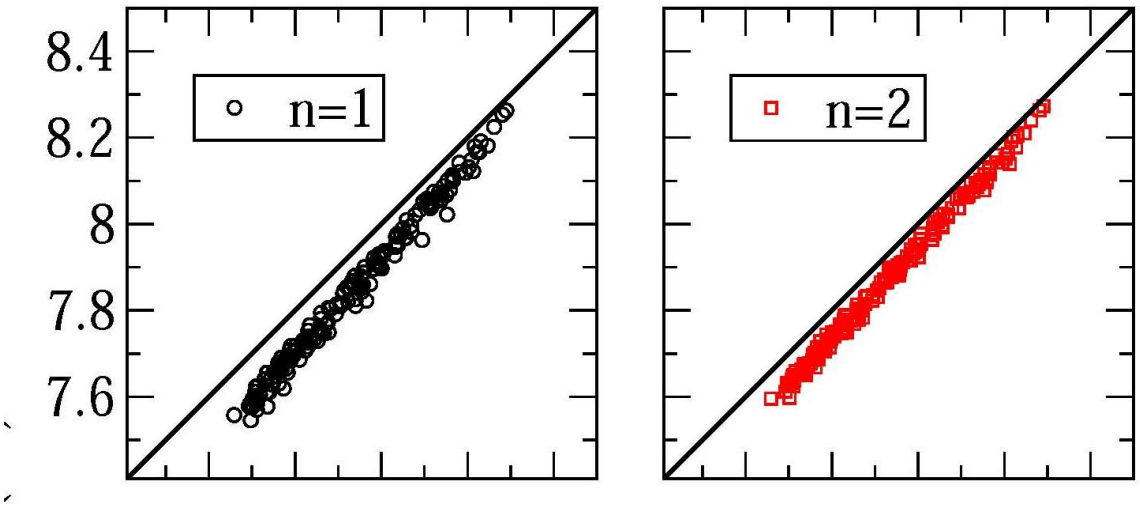
$$H\psi_i = \varepsilon_i\psi_i$$

$$(H-\varepsilon_{ref})^2\psi_i = (\varepsilon_i-\varepsilon_{ref})^2\psi_i$$

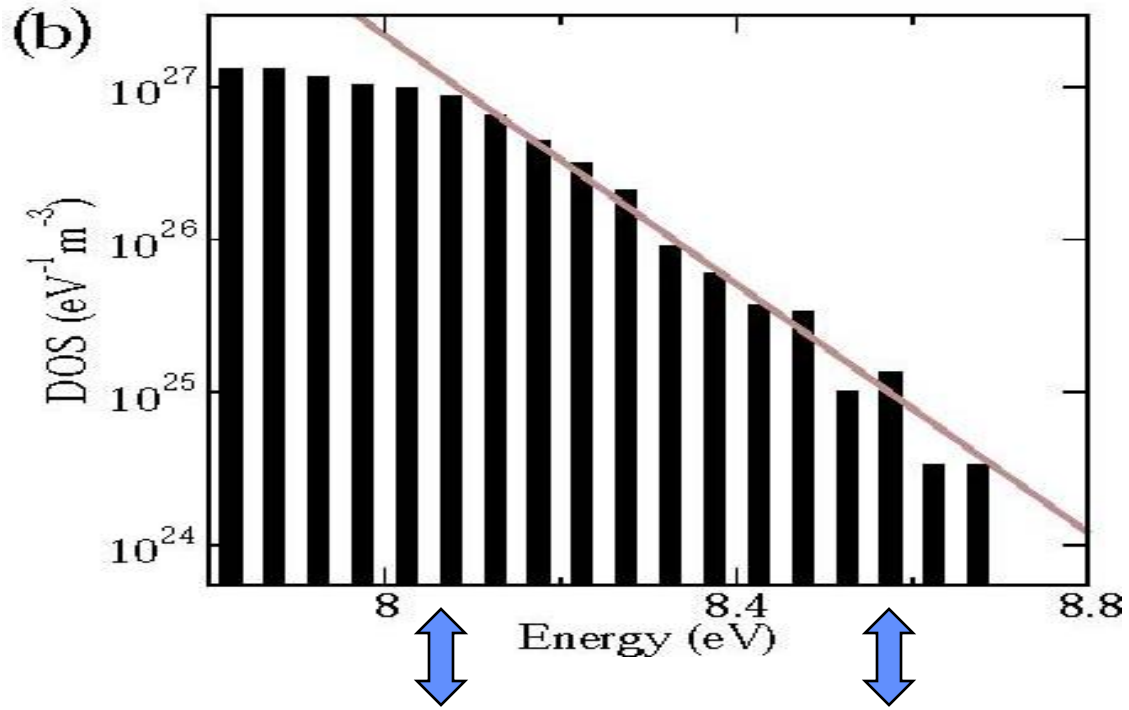
Calculating the electronic states using fragment basis

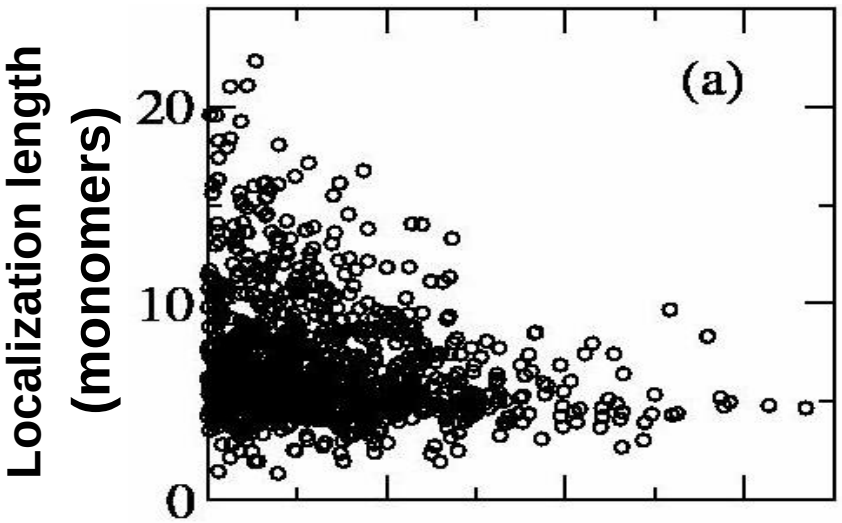
- Generate the basis set on each trimer of the thiophene rings
- The trimers are overlapping with each others.
- The number of basis set equal to the number of thiophene rings (or by x2, x3)
- But each trimer fragments cut from the system have to be calculated.





The density of the tail states





Averaged over 50 configurations (MD snapshots), and each with 10,000 atoms.

$$L = \frac{1}{\int \psi^4 d^3 r}$$

What causes the state localization at the DOS tail?

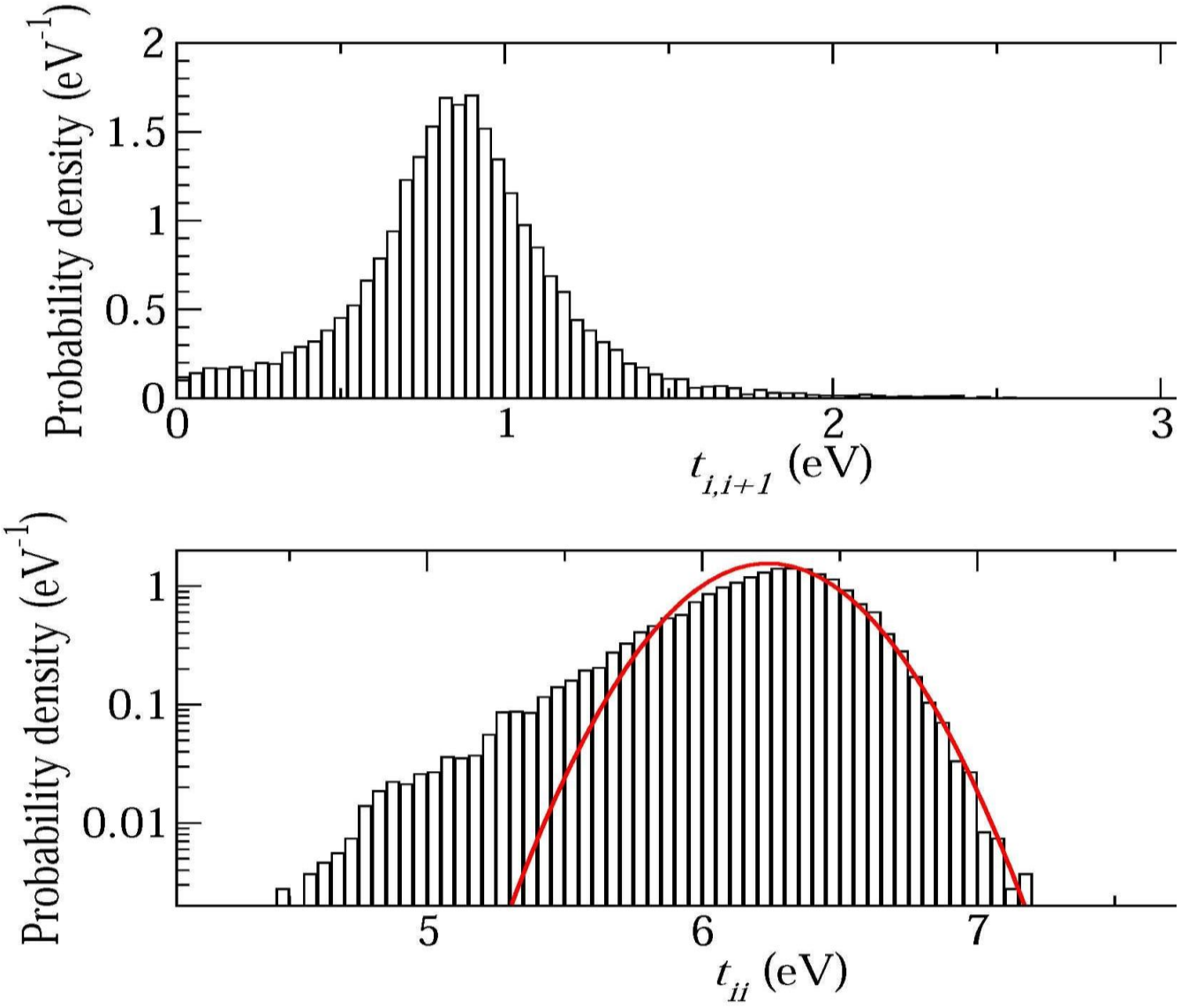
- The widely used common assumption (often based on tight-binding model) is that the localization is due to ring-ring torsion angle rotation.

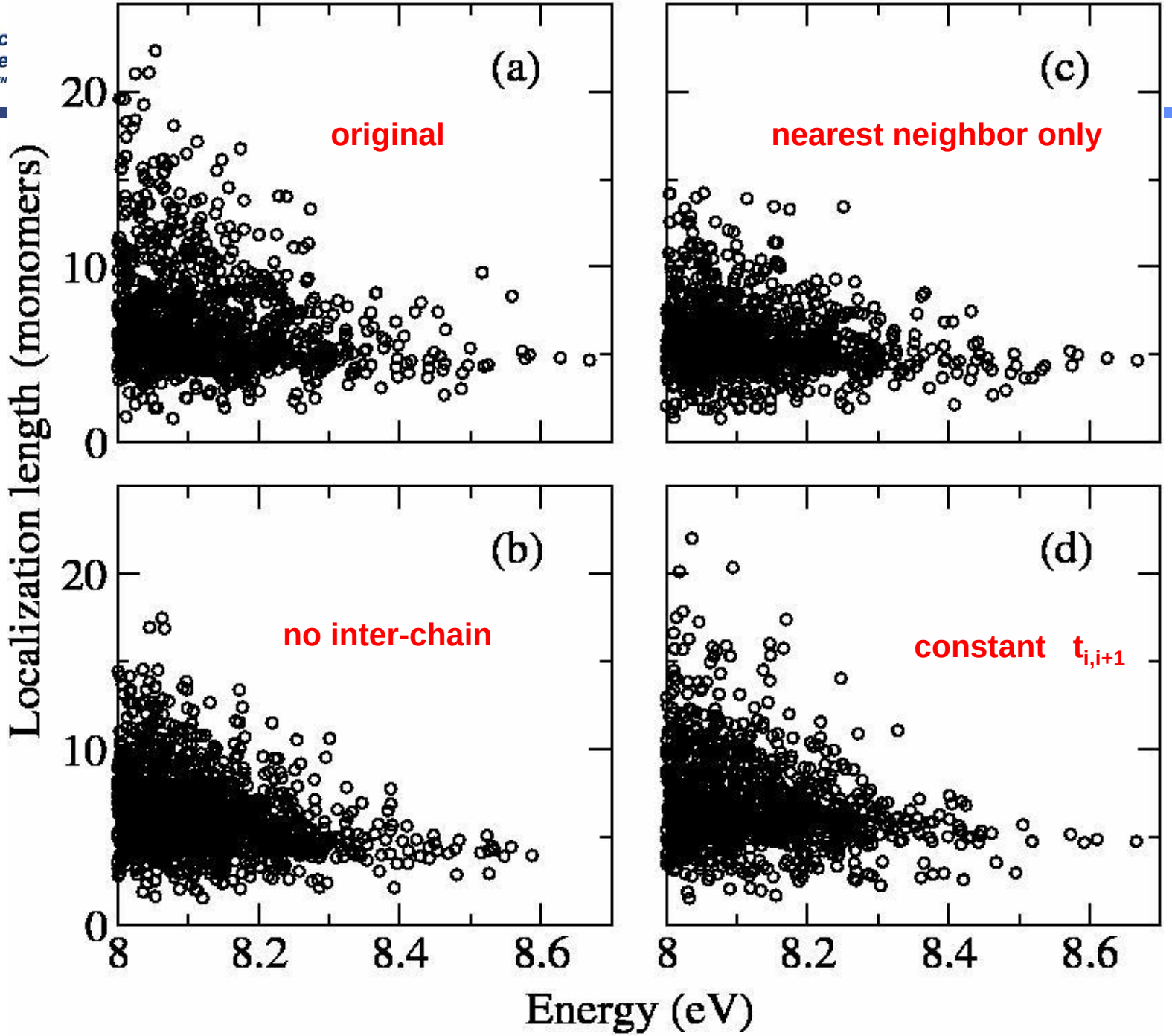
  According to this model, the DOS tail states should be extended states (correspond to long straight chains).

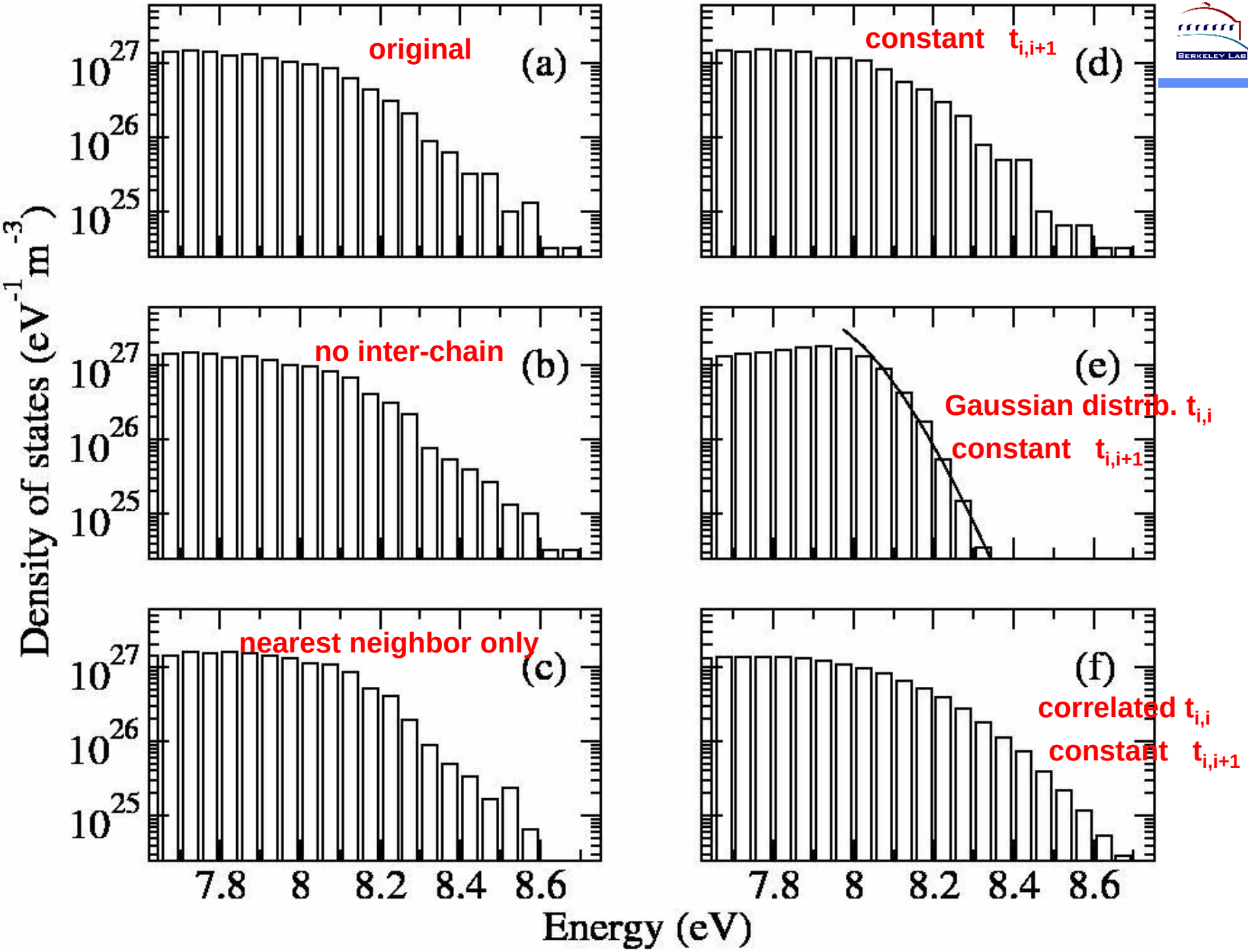
  But that contradict to our finding, in our result, the DOS tail states are more localized than the other states

- We have an alternative model: the localization is due to on site potential fluctuation due to the electrostatic interaction of nearby polymers. Thus, this cannot be described by simple tight-binding model.

The onsite and nearest neighbor TB constant t_{ij}




(a)
original
(c)
nearest neighbor only
(b)
no inter-chain
(d)
constant $t_{i,i+1}$
Localization length (monomers)
Energy (eV)
0
10
20
8
8.2
8.4
8.6


original
(a)
constant $t_{i,i+1}$
(d)
no inter-chain
(b)
(e)
Gaussian distrib. $t_{i,i}$
constant $t_{i,i+1}$
nearest neighbor only
(c)
(f)
correlated $t_{i,i}$
constant $t_{i,i+1}$
Density of states ($eV^{-1} m^{-3}$)
10^{27}
10^{26}
10^{25}
7.8
8
8.2
8.4
8.6
Energy (eV)

What cause the state localization ?

- A widely held view is that the localization is caused by torsion angle rotations

- We found that: the localization is due to chain-chain electrostatic interactions, which causes onsite potential fluctuations, much like the Anderson localization

Outline

(1) Hole hopping transport in random P3HT polymer

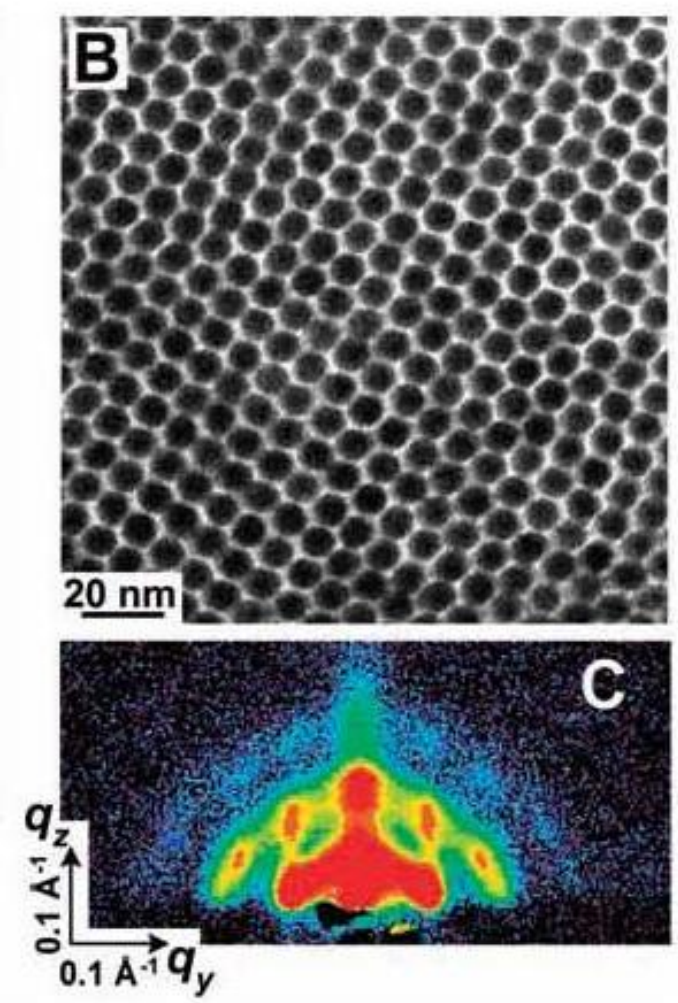
(2) Electron transport between connected quantum dots

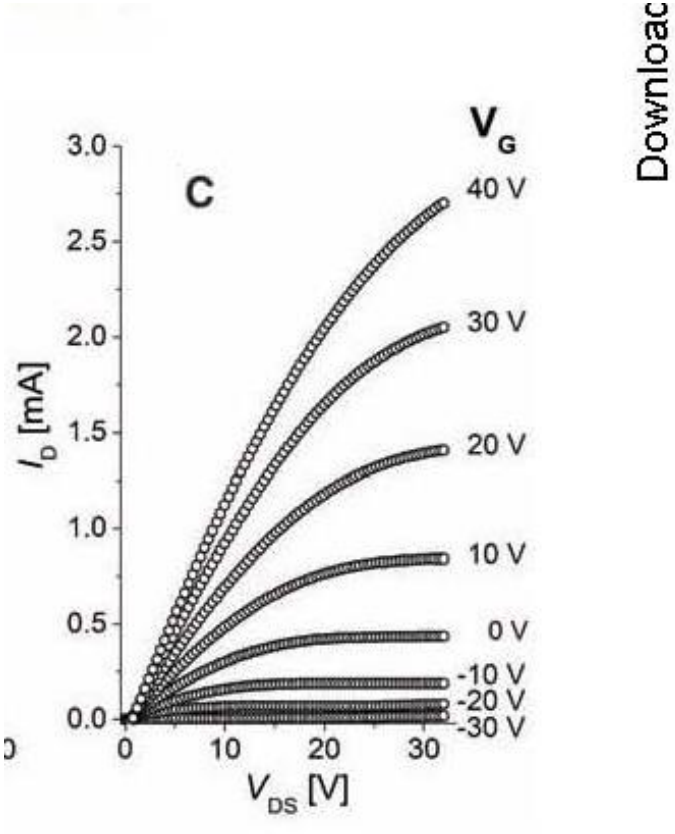
(3) Time-domain simulations

Acknowledgment

Nenad Vukmirovic (P3HT polymer)
Iek Heng Chu, Marina Radulaski (QD-QD transport)
Jifeng Ren (time domain simulation)

CdSe quantum dot array, connected by Sn_2S_6 molecule



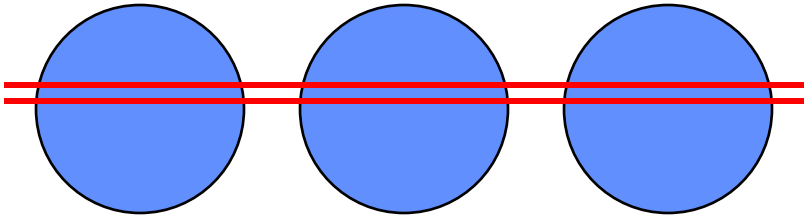


Downloac

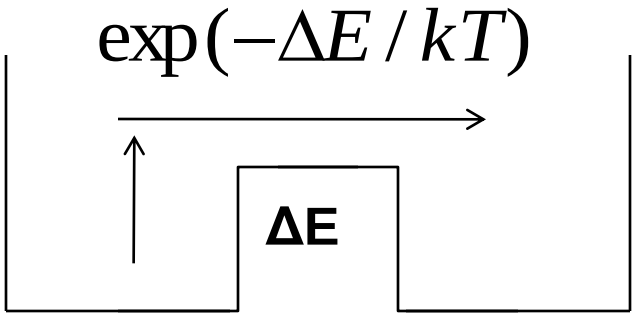
Talapin, et.al, Science (2005); Kovalenko, et.al, Science (2009).

What cause the electron transport ?

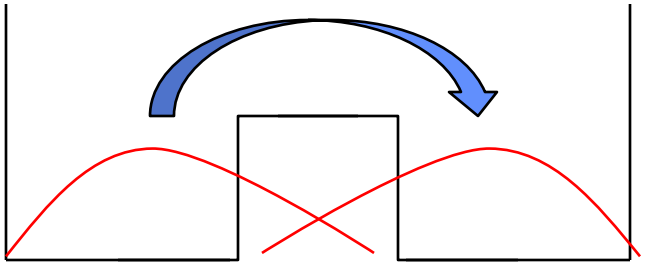
(1) Mini-band bulk like transport:



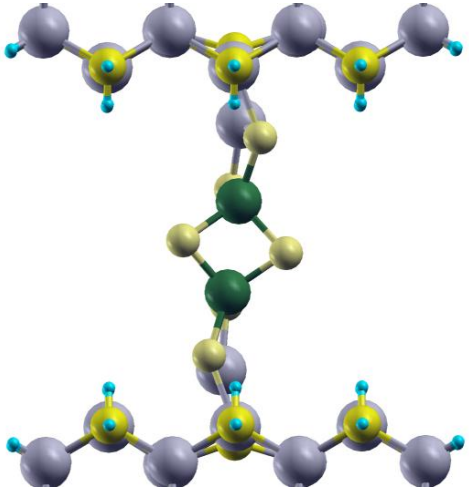
(2) Thermo activation, over the barrier
(like the Schottky barrier)

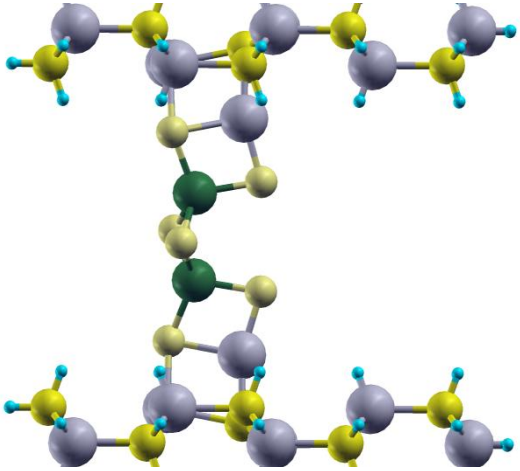


(3) Phonon assisted hopping
(e.g., described by Marcus theory)



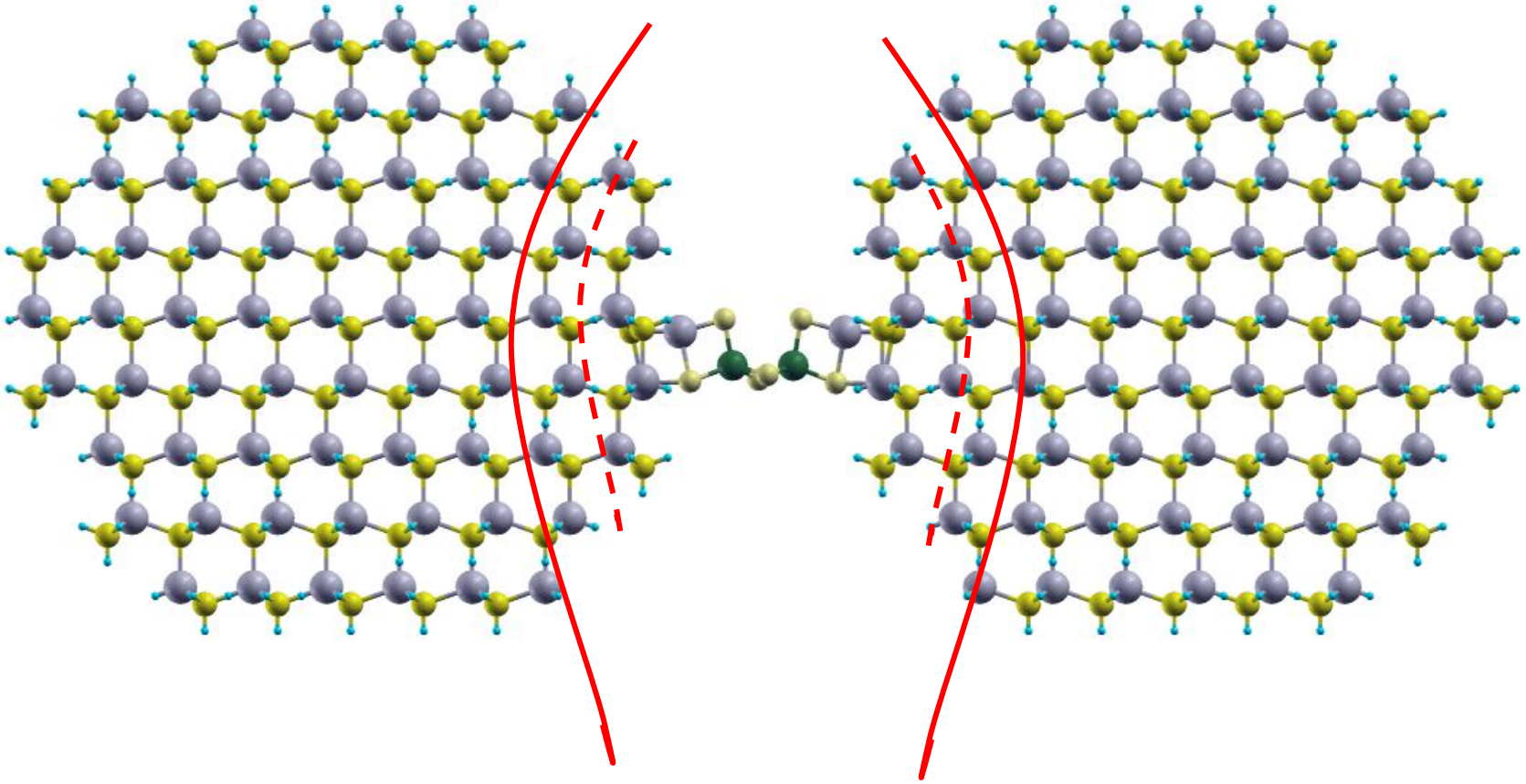
Sn_2S_6 atomic attachment to CdSe surfaces





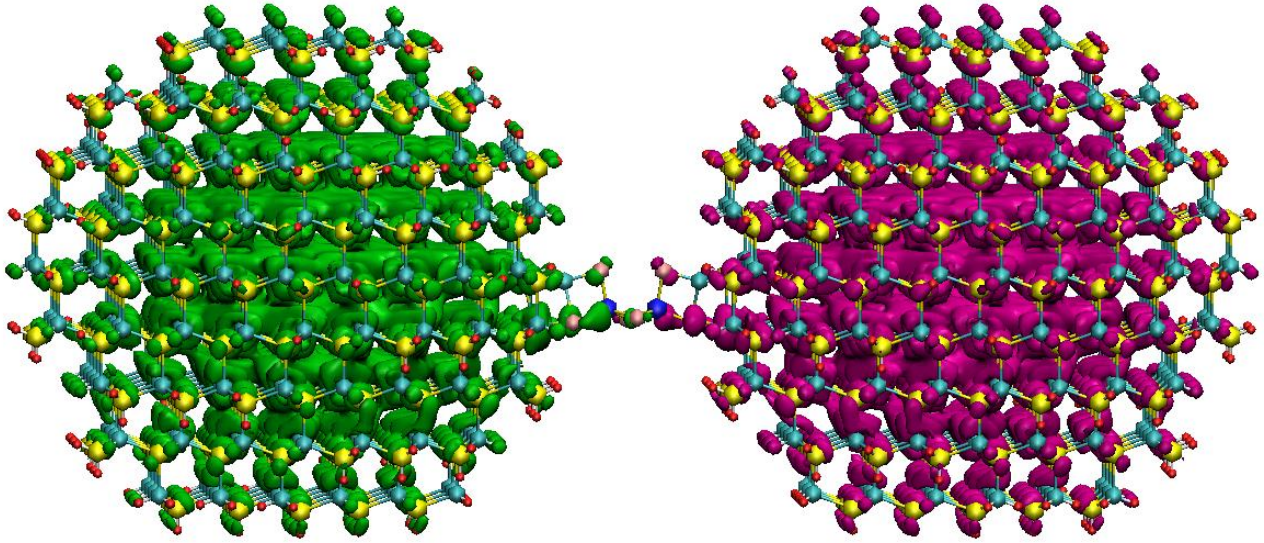
Flat surface calculation for the molecule attachment

Divide-and-conquer scheme to get the charge density

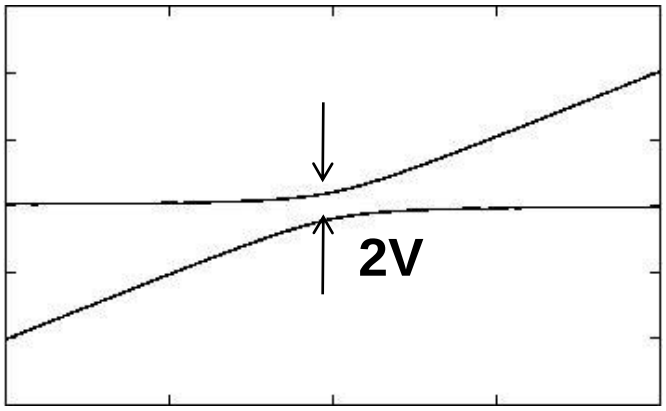


The electron coupling between the two states

CBM

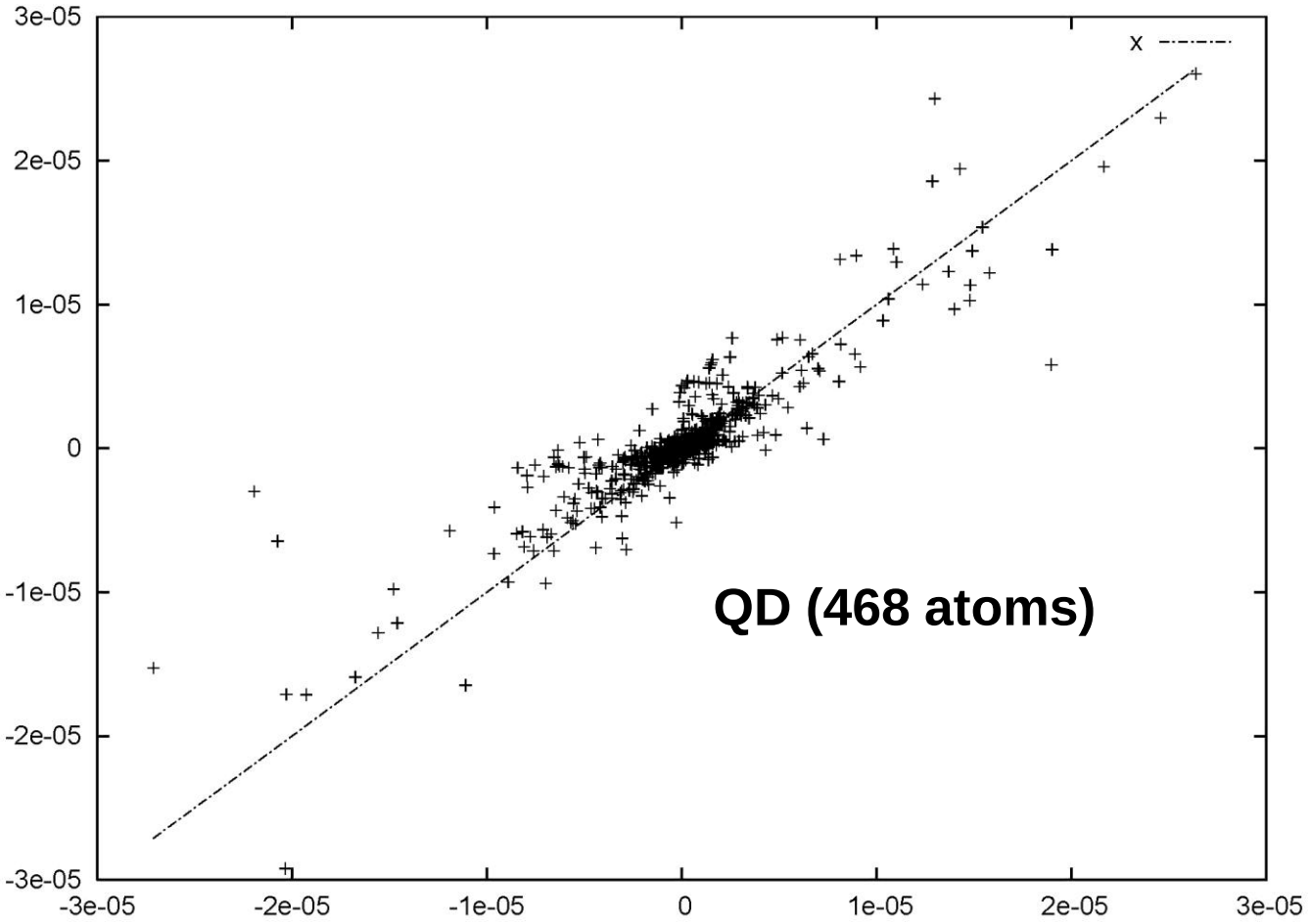


CBM+1



Natom	Size D (nm)	V (coupling meV)
468	2.5	4.1
1051	3.4	1.4
1916	4.3	0.37
3193	5.1	0.14

Charge patching method for electron-phonon coupling



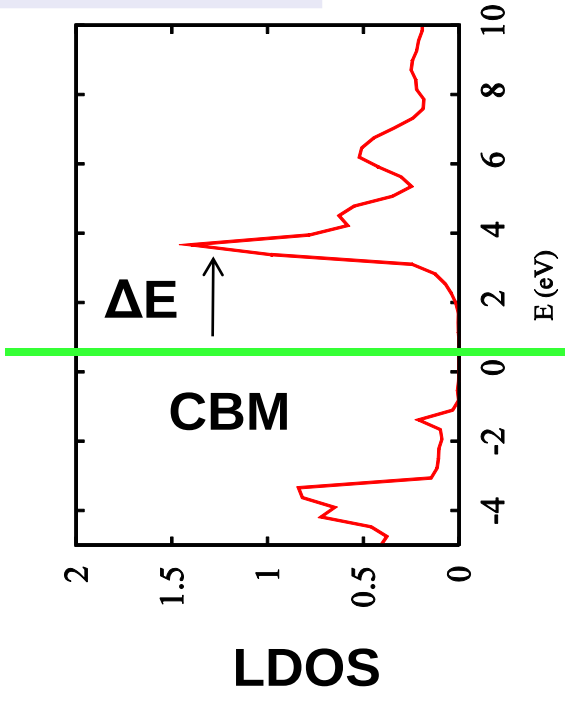
Calculating the re-organization energy

Natom	Size D (nm)	λ (re-org. energy, meV)	V (coupling meV, type I)
468	2.5	145	4.1
1051	3.4	62	1.4
1916	4.3	32	0.37
3193	5.1	23	0.14

(1) The λ >> V, so the wave function will be localized, it is not mini-band transport

(2) the barrier height ΔE can be ~ 2 eV. It cannot be over-the-barrier thermally excited transport.

(3) Must be phonon-assisted hopping transport



Calculating the transition rate

Marcus Theory

$$Rate = V_{ab}^2 \sqrt{\frac{\pi}{\lambda k T \hbar}} \exp[-(\lambda + \varepsilon_a - \varepsilon_b)^2 / 4\lambda k T]$$

Λ is the reorganization energy, Vab is the electron coupling constant, ε_a and ε_b are the onsite electron energies.

Quantum phonon treatment (G. Nan, et.al, Phys. Rev. B 79, 115203 (2009)):

$$Rate = \frac{1}{\hbar^2} |V_{ab}|^2 \int_{-\infty}^{\infty} dt \exp\left\{ i(\varepsilon_a - \varepsilon_b)t/\hbar - \sum_j S_j \left[(2n_j + 1) - n_j e^{-i\omega_j t} + (n_j + 1) e^{i\omega_j t} \right] \right\}$$

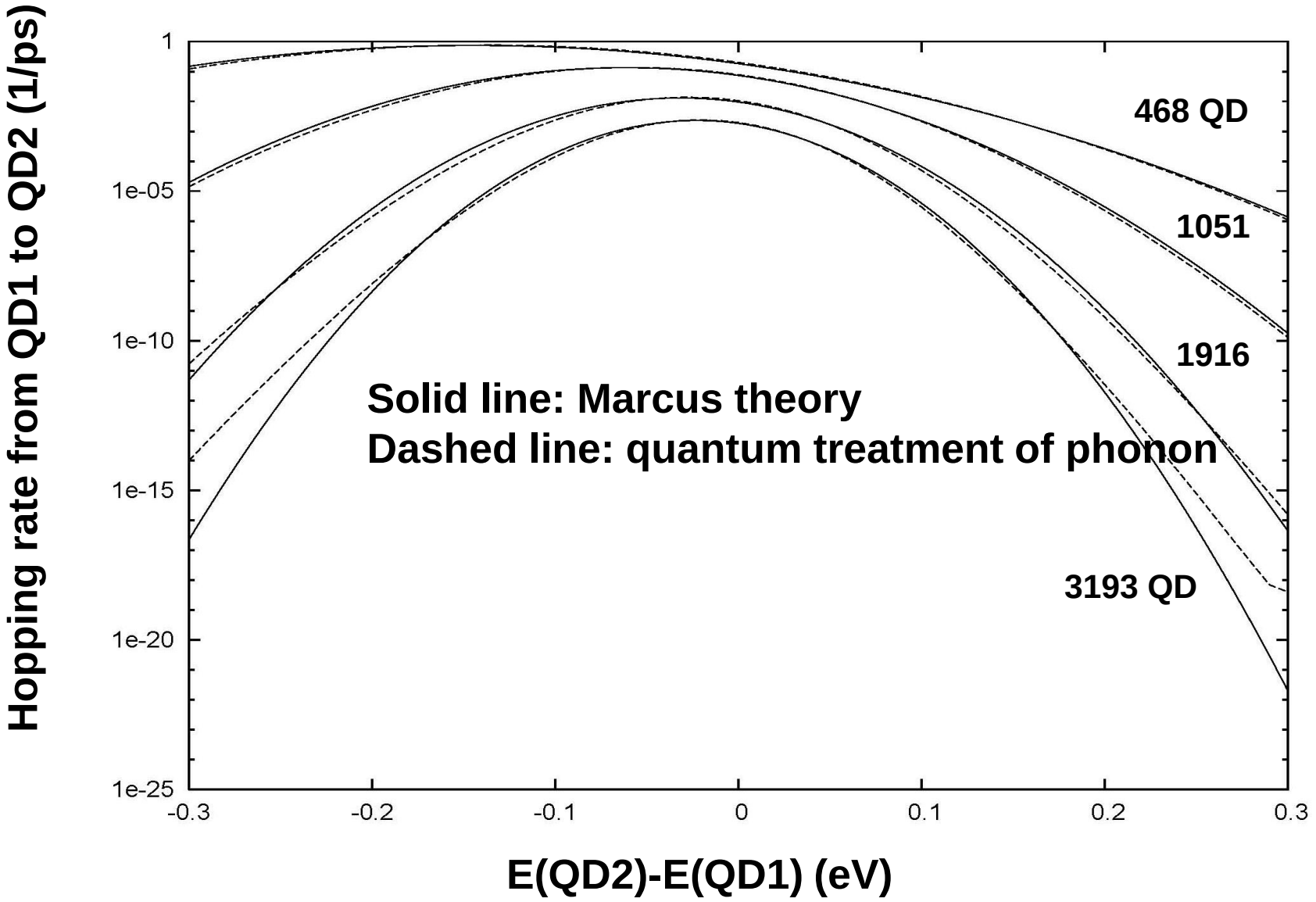
ω_j **is the phonon frequency,**

$n_j = 1/[\exp(\hbar\omega_j / k_B T) - 1]$ **is the phonon occupation**

$S_j = \lambda_j / \hbar\omega_j$ **is the Huang-Rhys factor for phonon mode j.**

The hopping rate

Attachment type I



Carrier mobility of the QD array in small carrier density limit

Situation (QD cubic array, size=4.3nm)	Type-I attachment Mobility μ ($cm^2/V/S$)
No QD size fluctuation, no connection fluctuation	8.22×10^{-2}
5% QD size fluctuation, no connection fluctuation	4.80×10^{-2}
5% QD size fluctuation, uniform connection fluctuation	1.02×10^{-2}
Experiment, size=4.5nm	3×10^{-2}

Outline

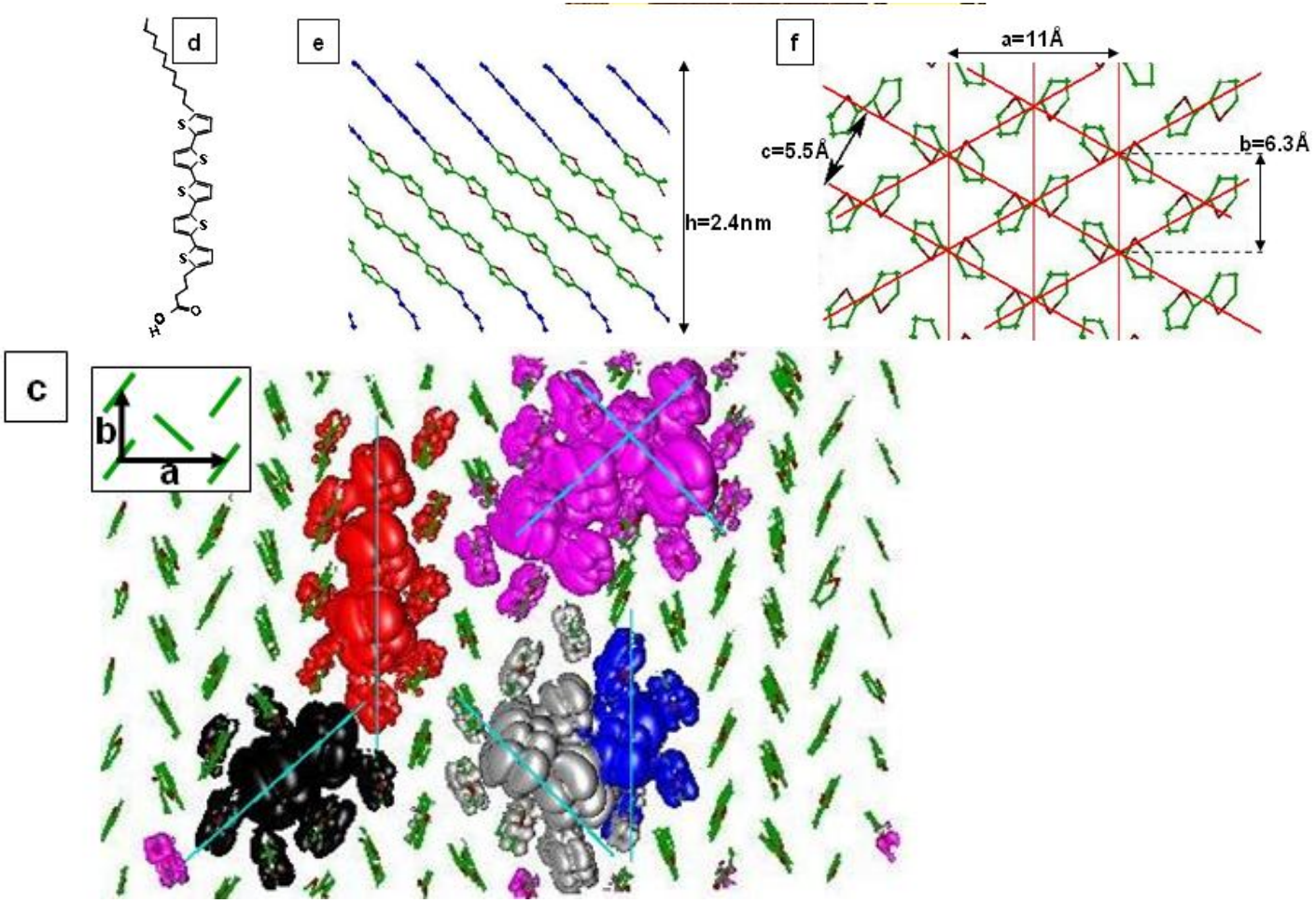
(1) Hole hopping transport in random P3HT polymer

(2) Electron transport between connected quantum dots

(3) Time-domain simulations

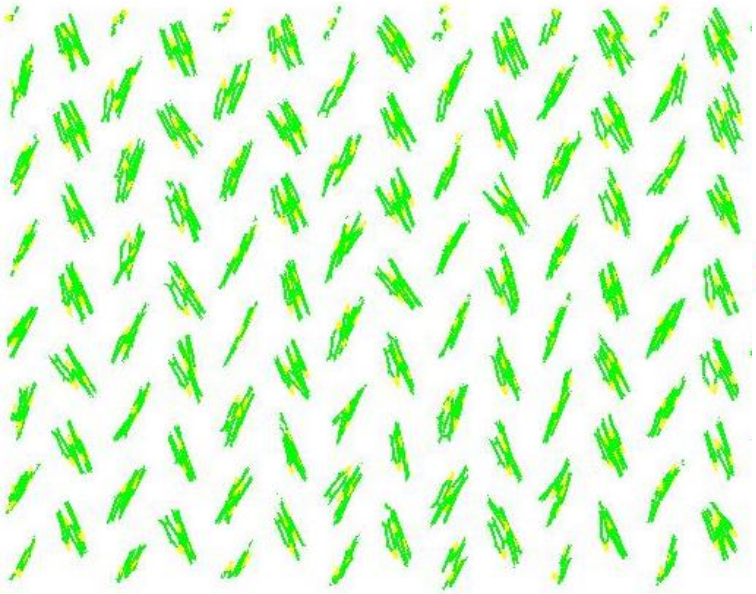
Acknowledgment

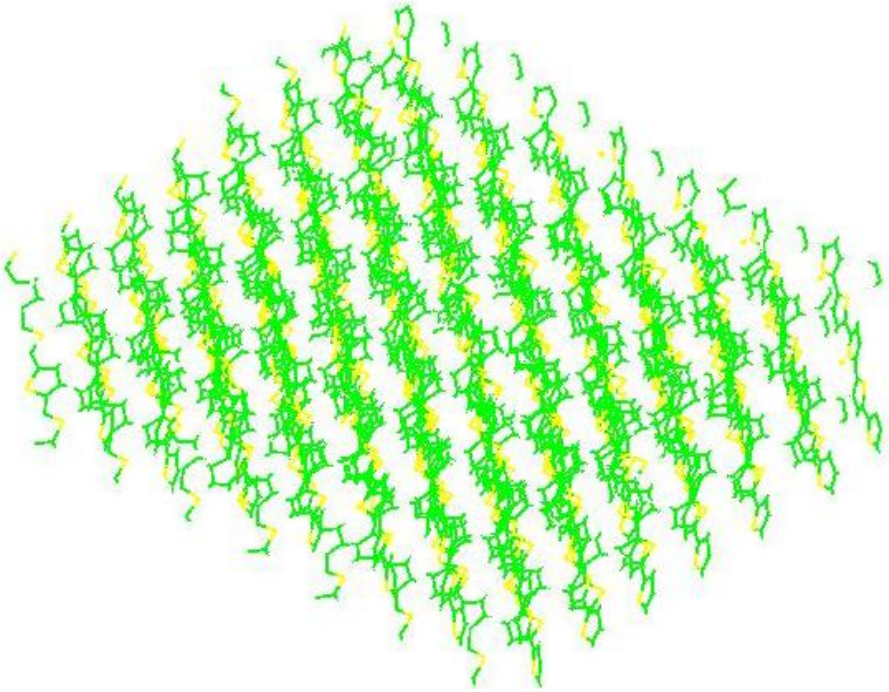
Nenad Vukmirovic (P3HT polymer)
Iek Heng Chu, Marina Radulaski (QD-QD transport)
Jifeng Ren (time domain simulation)

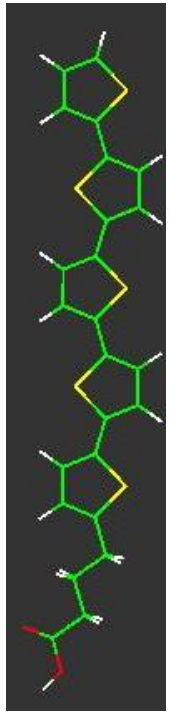


The molecular arrangement on a substrate and the corresponding hole wave functions at room temperature

One monolayer of D5TBA on a substrate





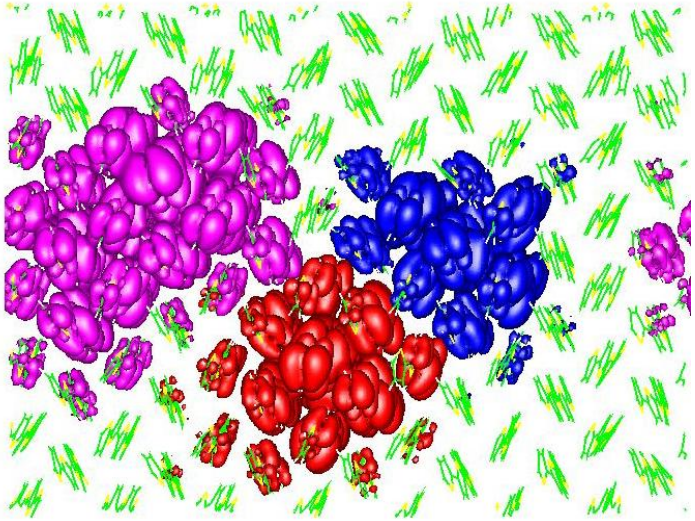


Herringbone structure

- The VFF structure agrees with experiments (after some fitting on VFF)
- Experiments are setting up to measure the in-plane mobility (M. Salmeron)
- There are some fundamental questions for carrier dynamics

Questions for the carrier dynamics

- Should we use phonon assisted state hopping to describe carrier mobility?
- Should we use Marcus theory (state crossing) ?
- Maybe the states will move with time (coherent transport).



Method to use:

A time-domain simulation can capture all these effects.

(1) $\ddot{R}(t) = mF$

(2) $i\dfrac{\partial}{\partial t}\psi(t) = H[R(t)]\psi(t)$

(3) some state collapses (dephasing)

Techniques and approximations

(1) Treat nuclei molecular dynamics (MD) with classical force field using LAMMPS

(2) Some special way to treat collapsing(not Tully algorithm)

(3) Obtain H[R(t)] using charge patching method (CPM)

(4) Solve the adiabatic eigen states $\phi_i(t)$ using overlapping fragment method (OFM).

Implications:

(1) Decouple the nuclei MD with electron dynamics, might have consequence for polaron effects (will be added later).

(2) Dephasing might be important (different algorithm will be tested later)

Solving the time dependent Schrodinger's equation

$$i\frac{\partial}{\partial t}\psi(t) = H[R(t)]\psi(t)$$

$$H[R(t)]\phi_i(t) = \varepsilon_i(t)\phi_i(t)$$

$$\psi(t) = \sum_i C(i,t)\phi_i(t)$$

$$\dot{C}(i,t) = -i\varepsilon_i(t)C(i,t) - \sum_j C(j,t)V_{ij}$$

$$V_{ij} = \left[\left\langle \phi_i(t) \middle| \phi_j(t+\Delta t)\right\rangle - \delta_{ij}\right]/\Delta t$$

Task: to calculate ϕ_i for many snapshots (Δt);
R(t) is already known from force field MD

What Δt one should use ?

- The mass of electron is thousand times smaller than mass of nuclei, should we use 10^{-3} fs for Δt ?

- Yes and No

- Yes: it is necessary to integrate

$$\dot{C}(i,t) = -i\varepsilon_i(t)C(i,t) - \sum_j C(j,t)V_{ij}$$ with $\Delta t = 10^{-3}$ fs.

- No: it is not necessary to solve $\phi_i(t)$ from

$$H[R(t)]\phi_i(t) = \varepsilon_i(t)\phi_i(t)$$ every 10^{-3} fs

- It is only necessary to solve $\phi_i(t)$ every fs. Within 1 fs, we can write:

$$H(t) = H(t_1) + (t - t_1)\Delta H$$

$$H(t) = H(t_1) + (t - t_1)\Delta H$$

- **Within $[t_1,t_2]$ (1 fs interval), if we assume**

$$\phi_i(t) = \sum_j D_i(j,t)\phi_j(t_1)$$

all we need to know is: $\langle \phi_i(t_1) | \Delta H | \phi_j(t_1) \rangle$

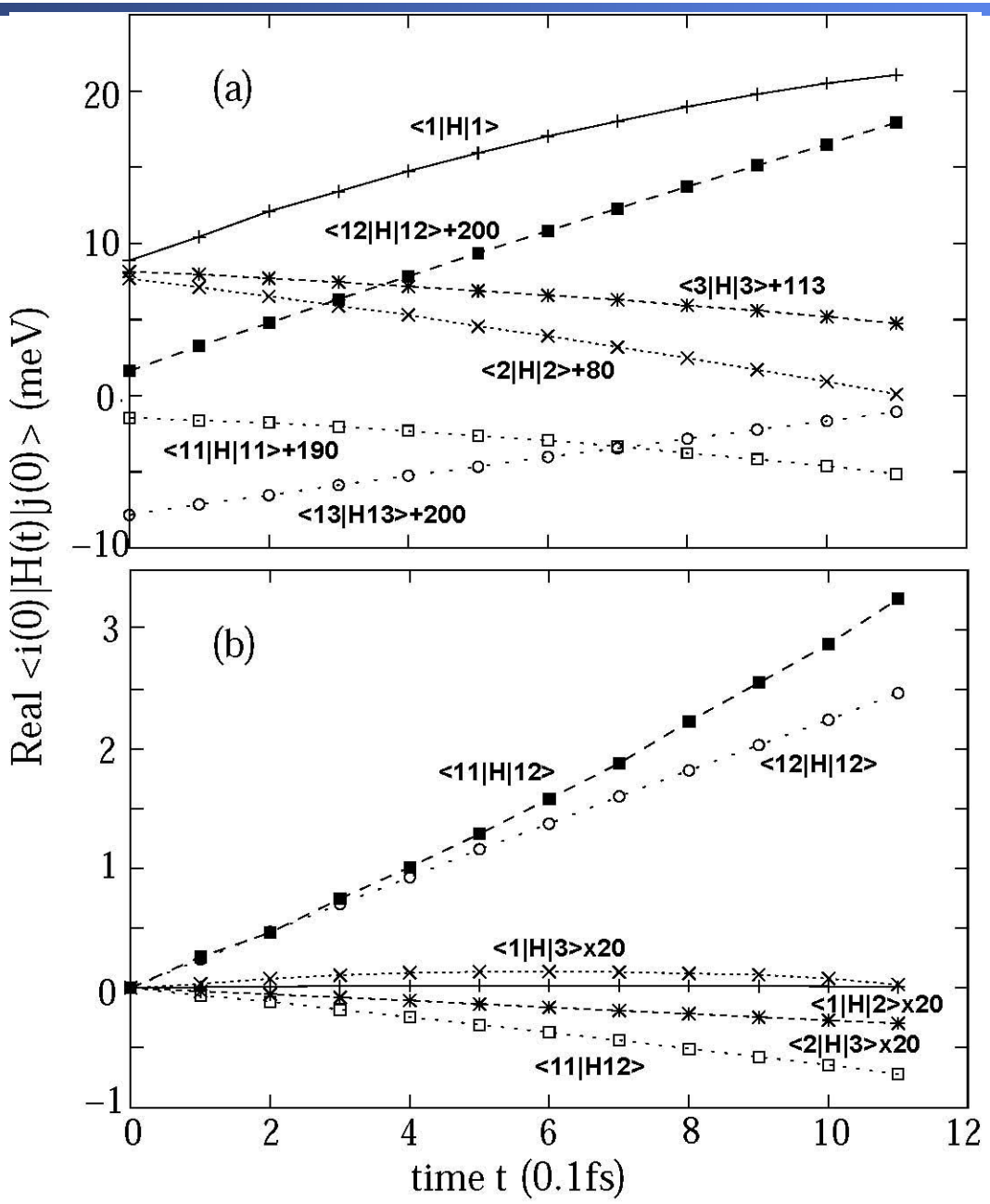
- **Then, within $[t_1,t_2]$, we only need to do a NxN matrix diagonalization, which is fast (N can be ~ 50).**

- **If we know $\phi_i(t_1)$ and $\phi_j(t_2)$, then we have:**

$$\langle \phi_i(t_1) | \Delta H | \phi_j(t_1) \rangle = \left\{ \sum_k \varepsilon_k(t_2) D(k,i) D^*(k,j) - \varepsilon_i(t_1) \right\} / (t_2 - t_1)$$

Here $D(k,i) = \langle \phi_k(t_2) | \phi_i(t_1) \rangle$

Linearity of ΔH

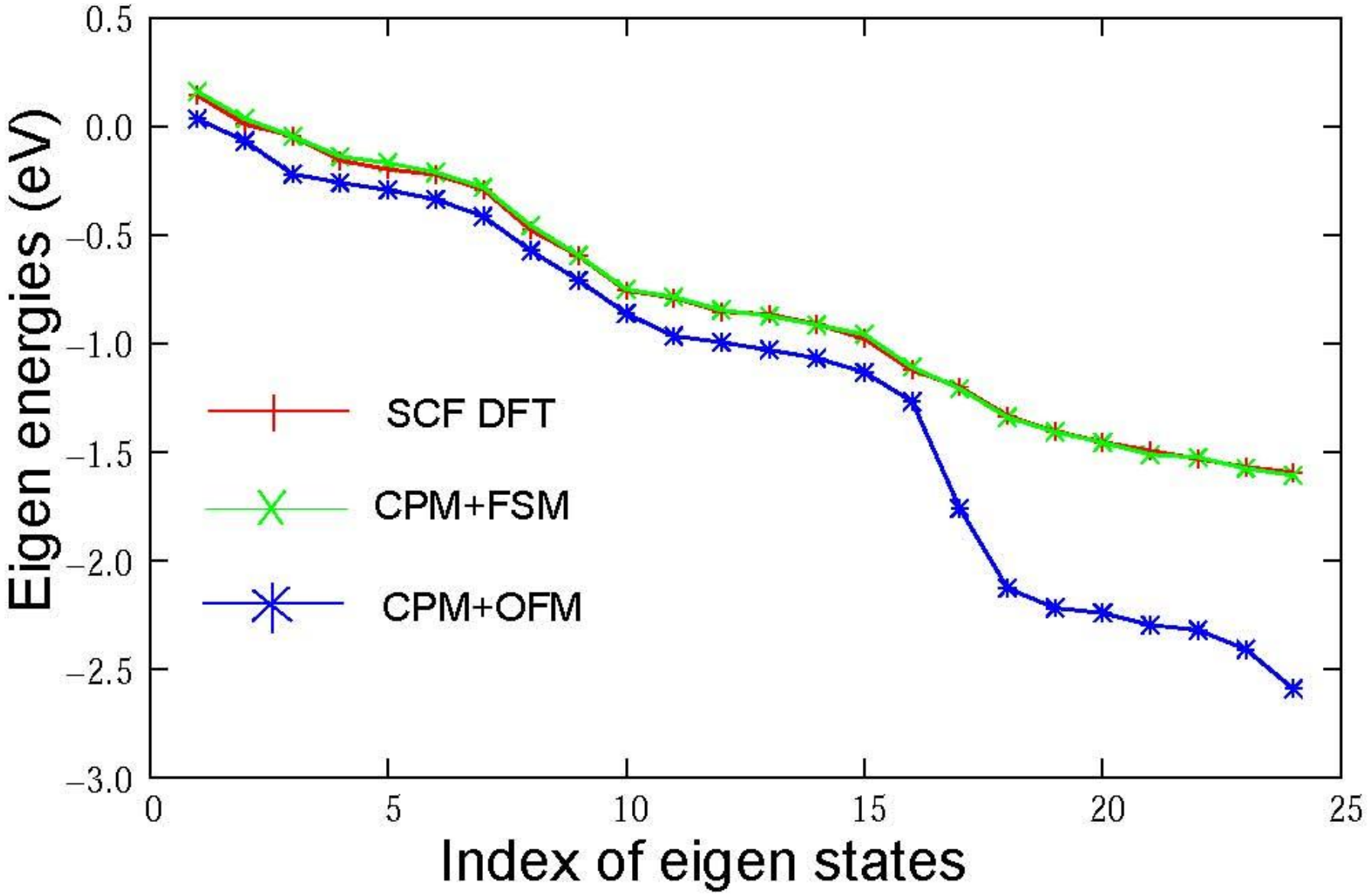


The quality of the charge patching method

	Method	VBM (eV)	VBM-1 (eV)	VBM-2 (eV)
2x2 relaxed	LDA	5.095	4.934	4.852
	CPM	5.092	4.932	4.850
2x2 MD snapshot1	LDA	5.153	5.008	4.944
	CPM	5.174	5.023	4.992
2x2 MD snapshot2	LDA	5.143	5.008	4.952
	CPM	5.158	5.034	4.953

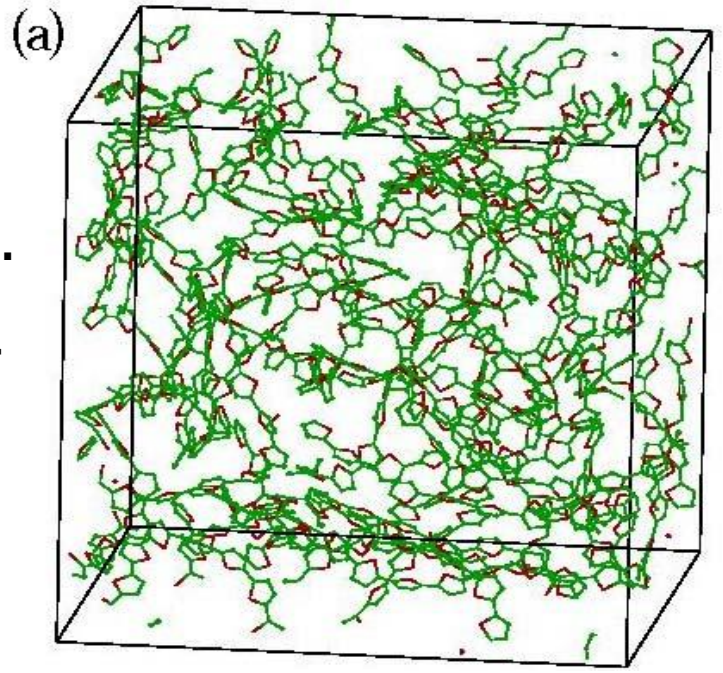
The charge patching method might have an error of 20-30 meV for each individual eigen energy

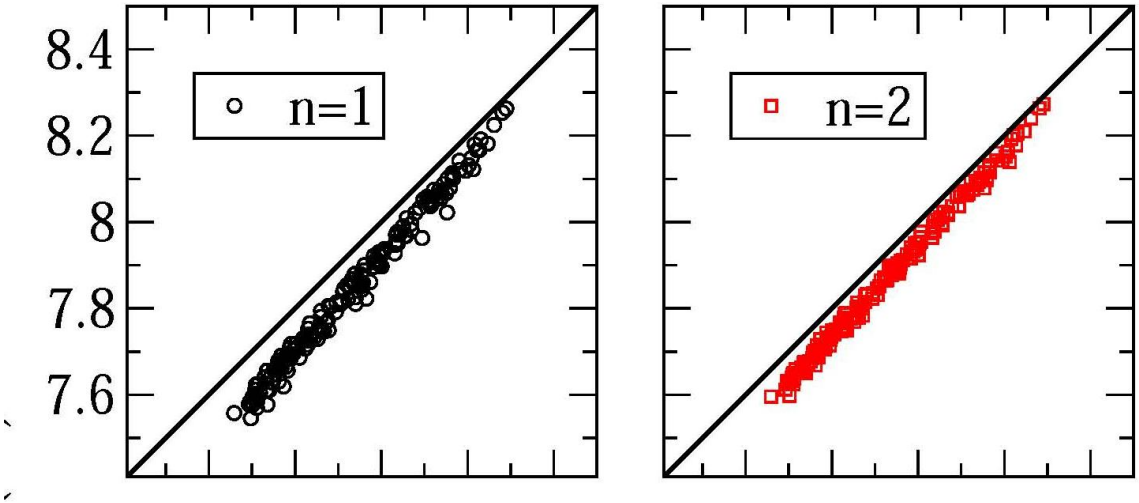
The overall density of state looks quite similar to LDA

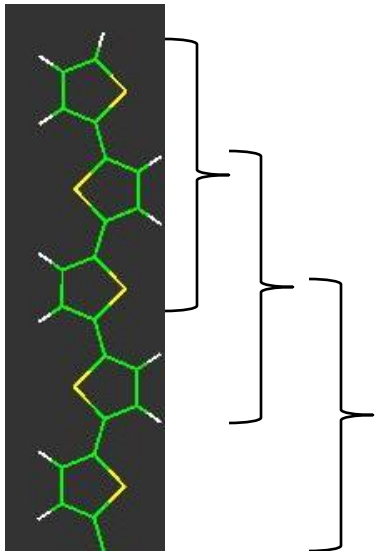

Eigen energies (eV)
0.5
0.0
−0.5
−1.0
−1.5
−2.0
−2.5
−3.0
0
5
10
15
20
25
Index of eigen states
SCF DFT
CPM+FSM
CPM+OFM

Calculating the electronic states using fragment basis

- Generate the basis set on each trimer of the thiophene rings
- The trimers are overlapping with each others.
- The number of basis set equal to the number of thiophene rings (or by x2, x3)
- But each trimer fragments cut from the system have to be calculated.



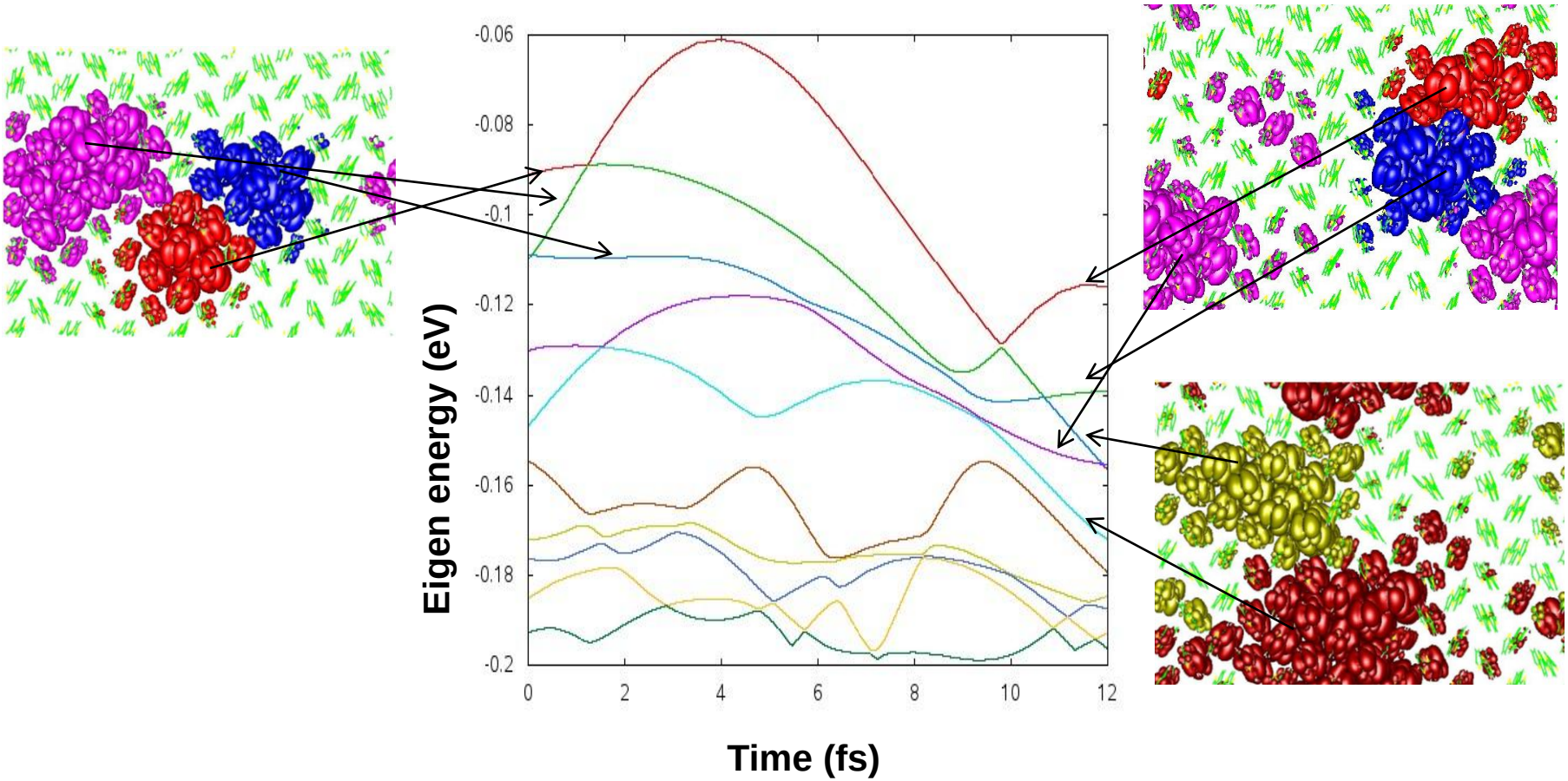




The computation: massive parallelization

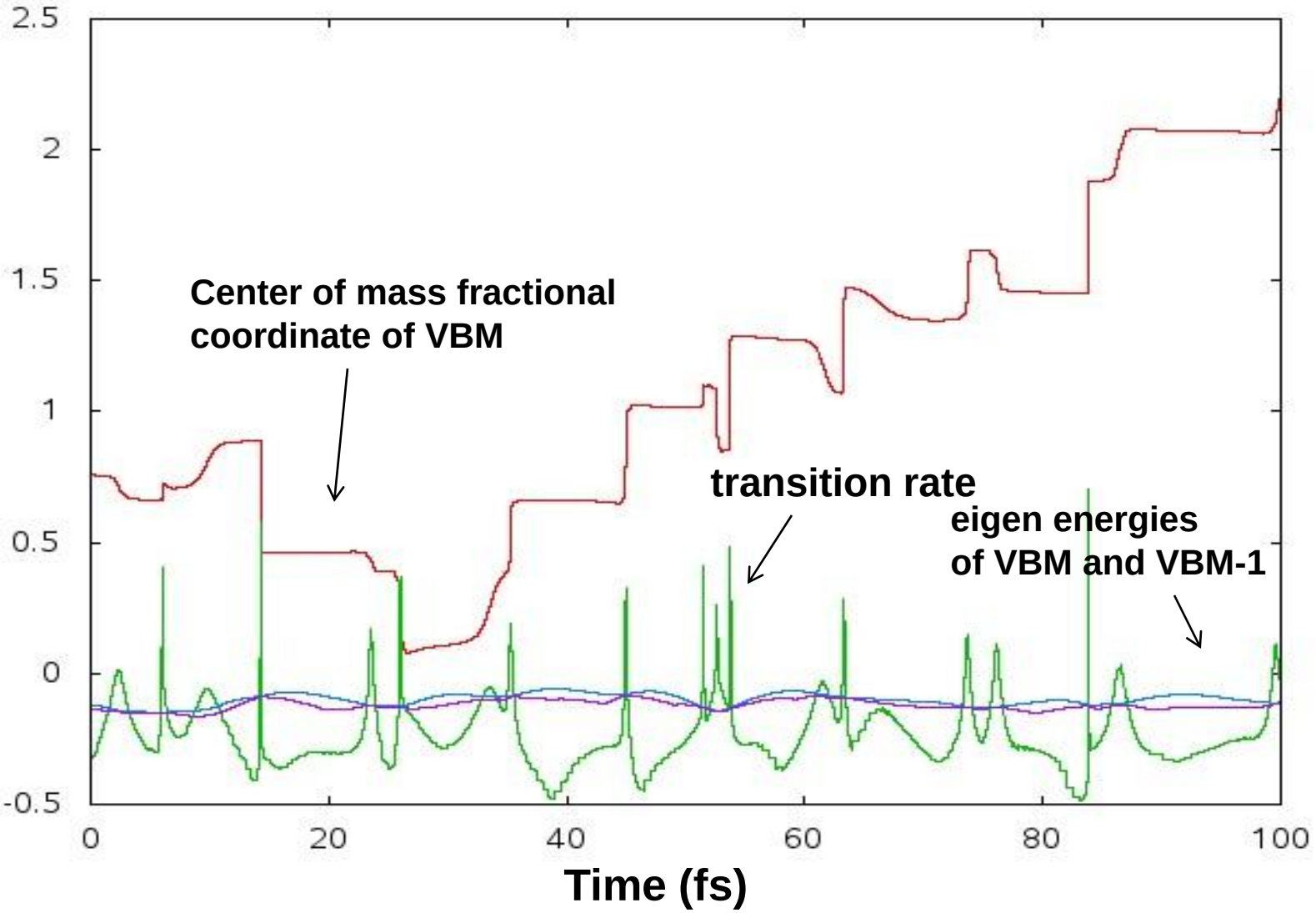
- One OFM takes 2352 CPU
- 2352 divided into 294 groups with 8 CPU in one group
- One group calculates one fragment
- One OFM job (2353 CPU) calculate 25 snapshots (0.5 fs apart), one after another
- 22 OFM jobs (51,744 CPU) calculate simultaneously on Jaguarpf
- 1650 snapshots (825 fs) take about 2 hours.

Eigen energies and eigen states



- One can trace the eigen states
- The state location might not change much, but its energy changes a lot (0.06 eV)

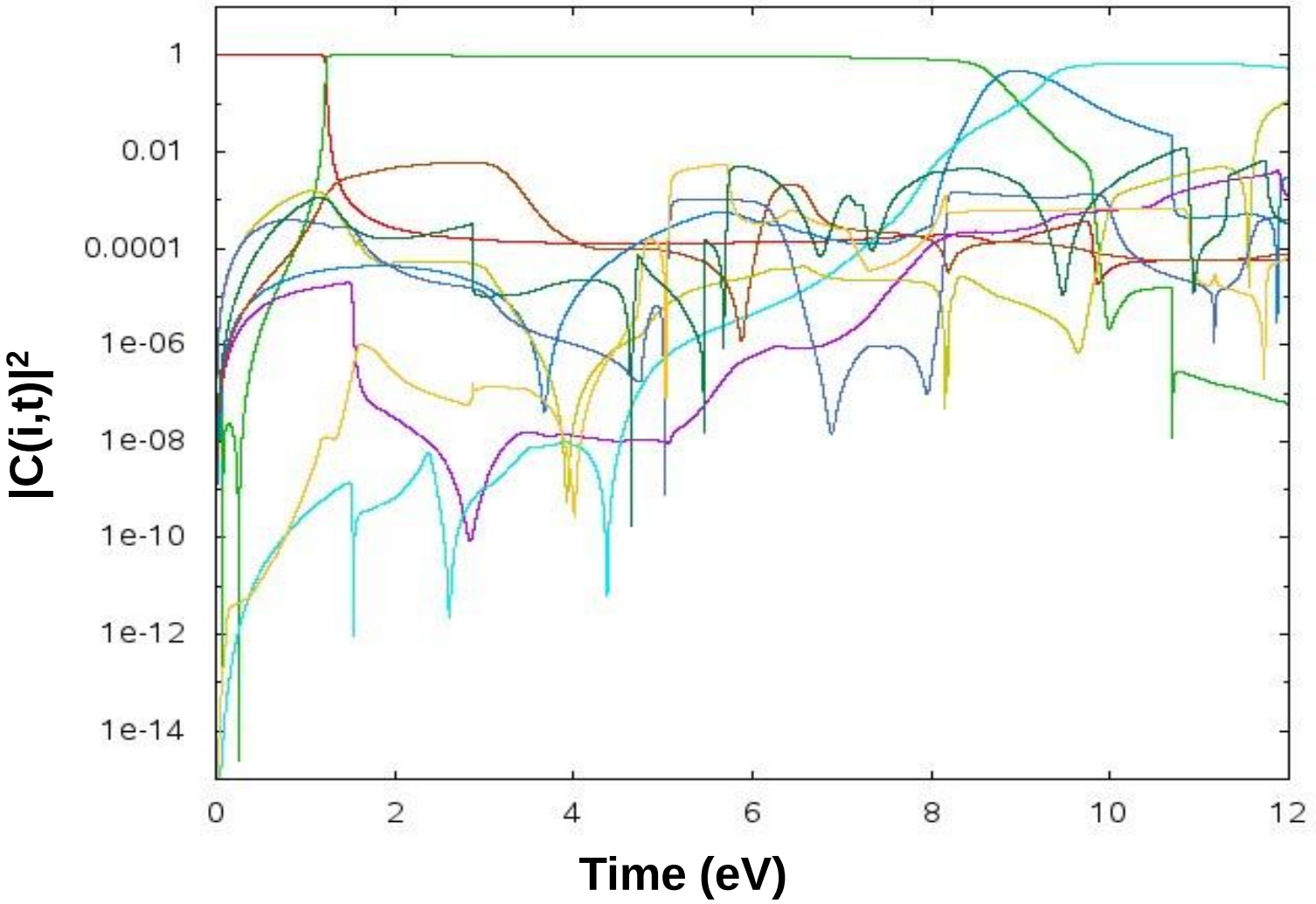
The eigen state positions



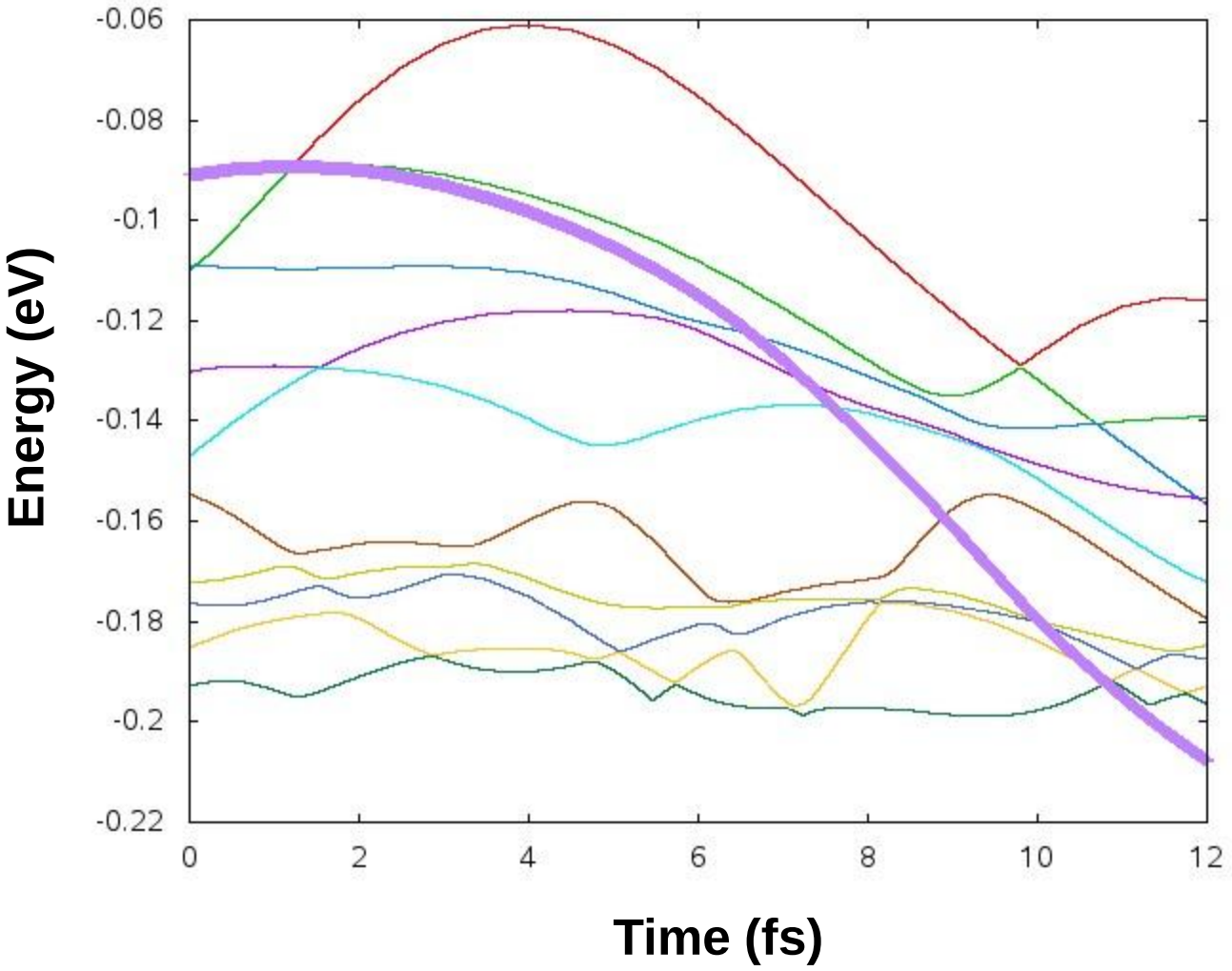
The drifting of eigen state positions are rather slow

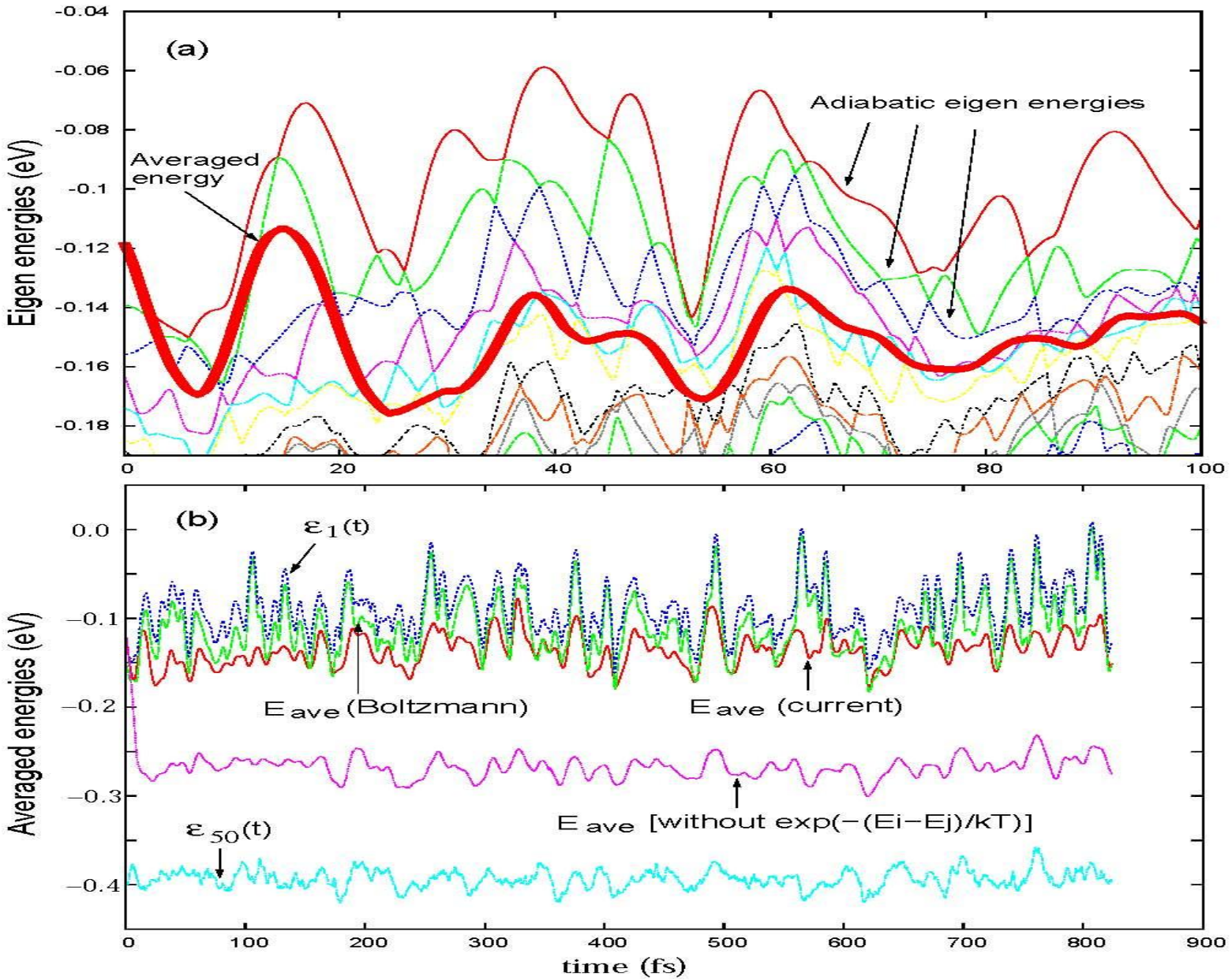
The coefficient $|C|^2$

$$\psi(t) = \sum_i C(i,t)\phi_i(t)$$



The energy change of a nonadiatic state



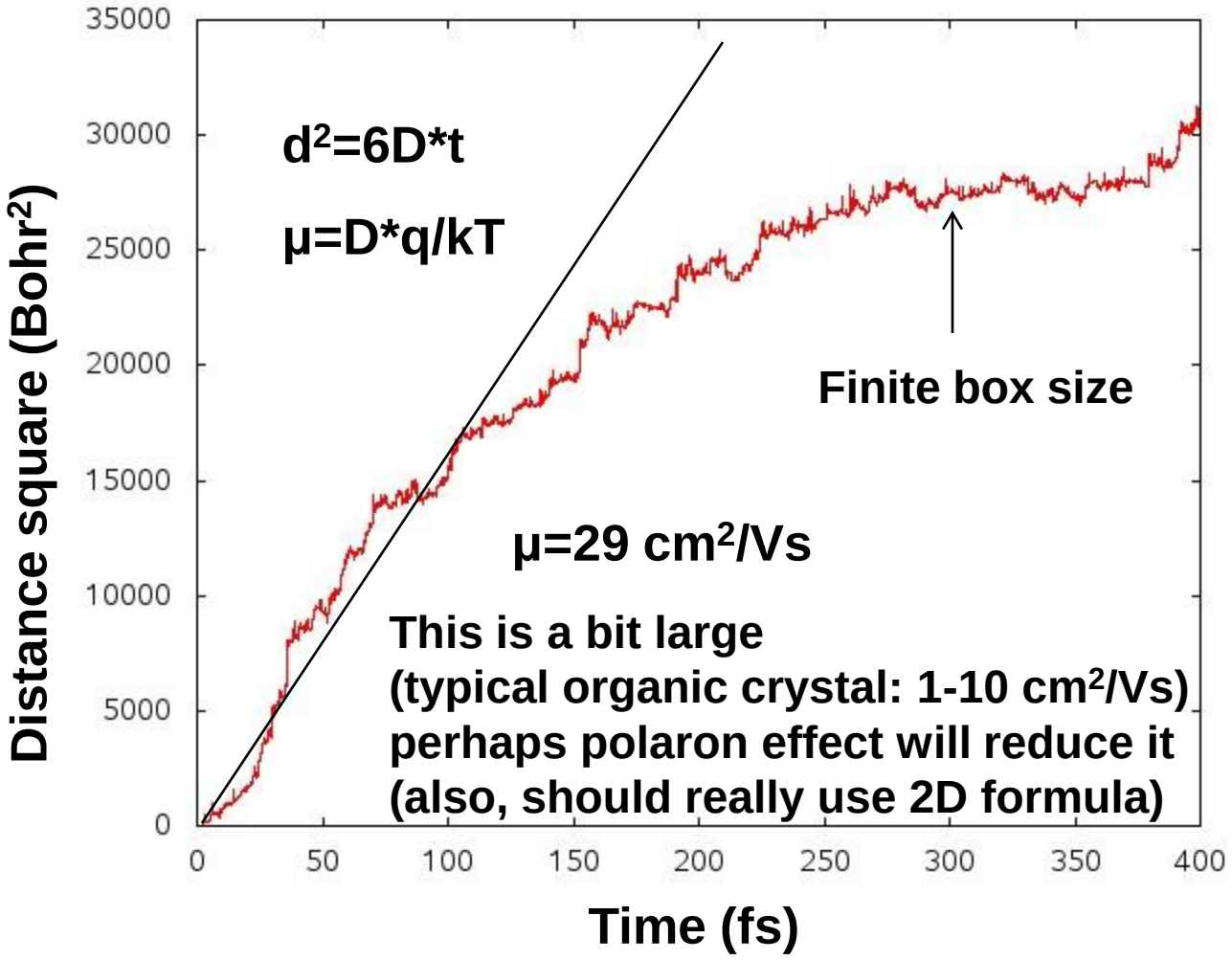

(a)
Averaged energy
Adiabatic eigen energies
Eigen energies (eV)
-0.04
-0.06
-0.08
-0.1
-0.12
-0.14
-0.16
-0.18
0
20
40
60
80
100
(b)
ε1(t)
E ave (Boltzmann)
E ave (current)
E ave [without exp(−(Ei−Ej)/kT)]
ε50(t)
Averaged energies (eV)
0.0
−0.1
−0.2
−0.3
−0.4
0
100
200
300
400
500
600
700
800
900
time (fs)

What is wrong?

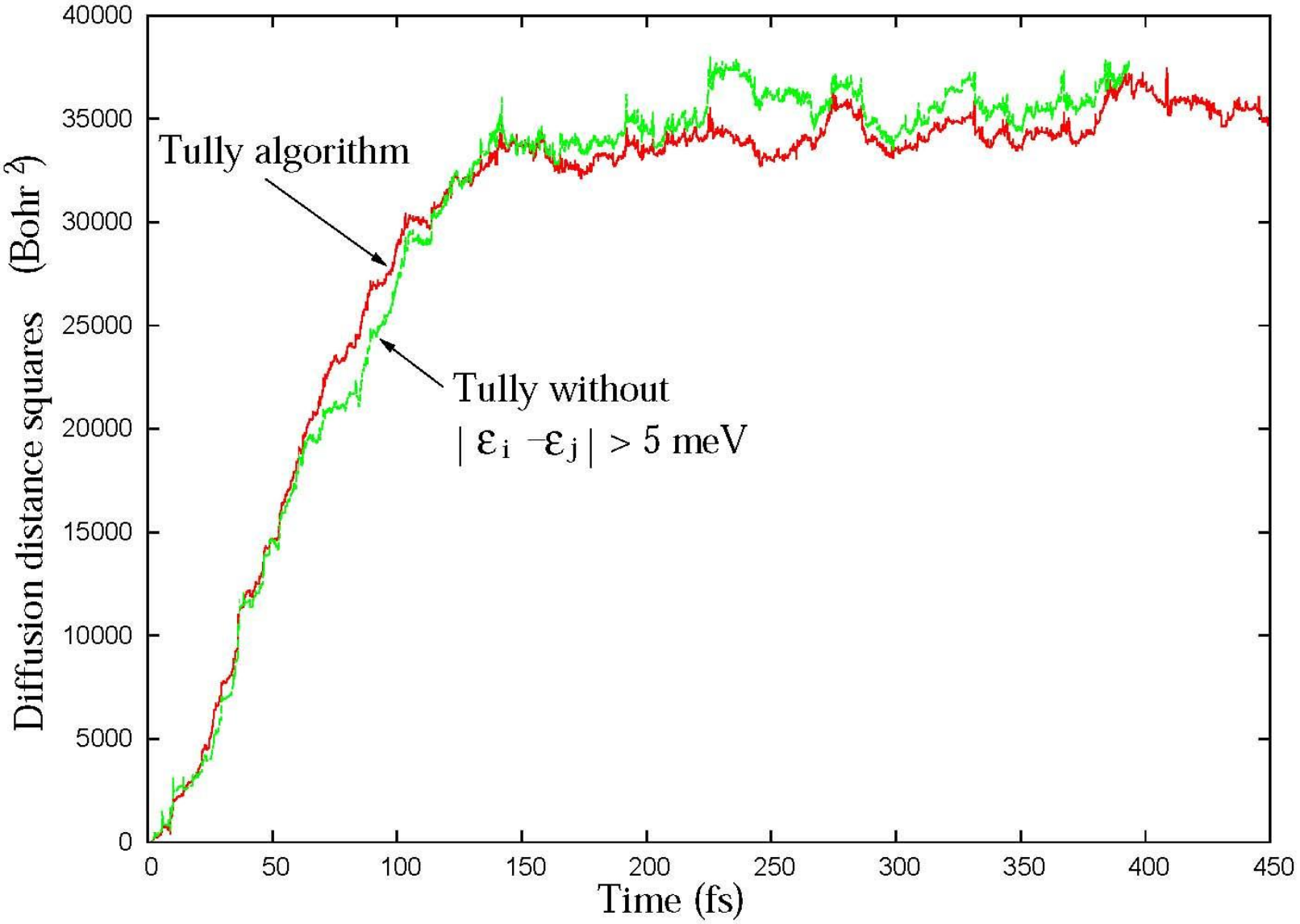
- The Boltzmann distribution is not maintained
- Not due to energy transfer between nuclei and electron, electron energy is small
- Nuclei movement is treated classically, no zero phonon movement, which is essential for Boltzmann distribution
- An empirical fix

$$\dot{C}(i,t) = -i\varepsilon_i(t)C(i,t) - \sum_j C(j,t)V_{ij} \times \begin{cases} \exp(-|\varepsilon_i(t) - \varepsilon_j(t)|/kT) \\ \text{If } \varepsilon_i < \varepsilon_j \text{ and i loses weight} \\ \text{or } \varepsilon_i > \varepsilon_j \text{ and i gains weight} \\ 1 \end{cases}$$

Diffusion distance



The effects of phonon absorption vs state crossing



CONCLUSION

- We have shown that it is okay to use 1fs step to do time-domain simulation.
- The equation needs to be changed to take into account the zero phonon effect, so Boltzmann dist. will held
- Currently, the electron and nuclei movements are decoupled. But they can be coupled together in a time-dependent DFT SC style calculation
- The calculated mobility seems a bit large, perhaps polaron effect will reduce this mobility
- The diffusion seems to be induced mostly by state crossing

CONCLUSIONS

(1) O(N) divide-and-conquer method can be used to calculate large nanostructures, but it is still expensive

(2) Charge patching method provides a cheap alternative

(3) Electron-phonon coupling can be calculated in disordered polymer to simulate the hole mobility

(4) QD-QD array carrier transport is due to phonon-assisted hopping

(5) Time-domain can be used to study carrier transport in a large organic system.